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ABSTRACT

The first section of this report describes the needs, objectives, and constraints of monitoring groundwater quality with particular emphasis on the problem as viewed by the United States Environmental Protection Agency, given its legislative mandates in the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500), and the Safe Drinking Water Act of 1974 (PL 93-523). The second section develops a methodology for monitoring groundwater quality degradation resulting from man's activities. The methodology is presented in the form of a series of procedural steps arranged in chronological order. By so doing, a straightforward sequence of actions is outlined which can lead to a groundwater pollution monitoring program in a given area. The third and final section of the report provides information on groundwater quality. A description is given of the geologic framework governing the movement of groundwater, and natural underground water quality. The occurrence of groundwater pollution, including its distribution, mechanisms, attenuation, evaluation, and trends is presented. The constituents in polluted groundwater and the various sources and causes of pollution are reviewed. The section ends with a discussion of water quality in relation to water use.

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TABLE OF CONTENTS

Page

ABSTRACT iii
ACKNOWLEDGEMENTS iv
LIST OF FIGURES vii
LIST OF TABLES xi
SECTION I — INTRODUCTION 1
  BACKGROUND AND SCOPE 1
    Monitoring Groundwater Quality: Methods and Costs 2
    Monitoring Groundwater Quality: Data Management 2
    Monitoring Groundwater Quality: Economic Framework and Principles 2
    Monitoring Groundwater Quality: Illustrative Examples 3
  PURPOSE AND APPROACH 4
    Ambient Trend Monitoring 4
    Source Monitoring 4
    Case Preparation Monitoring 5
    Research Monitoring 5
  NEEDS AND OBJECTIVES 5
    Economic Needs and Objectives 5
    EPA Needs and Objectives 8
    Monitoring Objectives 11
  CONSTRAINTS 13
SECTION II — MONITORING METHODOLOGY 15
  CONCEPT OF A MONITORING METHODOLOGY 15
  IMPLEMENTATION OF A MONITORING METHODOLOGY 16
    Step 1 — Select Area or Basin for Monitoring 16
    Step 2 — Identify Pollution Sources, Causes and Methods of Waste Disposal 20
    Step 3 — Identify Potential Pollutants 25
    Step 4 — Define Groundwater Usage 32
    Step 5 — Define Hydrogeologic Situation 34
    Step 6 — Study Existing Groundwater Quality 39
    Step 7 — Evaluate Infiltration Potential of Wastes at the Land Surface 42
    Step 8 — Evaluate Mobility of Pollutants from the Land Surface to Water Table 46

CONTENTS (continued)

Page

Step 9 — Evaluate Attenuation of Pollutants in the Saturated Zone 51
Step 10 — Prioritize Sources and Causes 54
Step 11 — Evaluate Existing Monitoring Programs 57
Step 12 — Establish Alternative Monitoring Approaches 58
Step 13 — Select and Implement the Monitoring Program 64
Step 14 — Review and Interpret Monitoring Results 65
Step 15 — Summarize and Transmit Monitoring Information 65

SECTION III — GROUNDWATER QUALITY 84
HYDROGEOLOGIC FRAMEWORK 84
Geologic Formations as Aquifers 84
Groundwater Movement 86
Natural Chemical Quality 87
OCCURRENCE OF GROUNDWATER POLLUTION 91
Definition 91
Distribution of Pollutants 91
Mechanisms of Pollution 92
Attenuation of Pollution 104
Distribution of Pollution Underground 106
Evaluation of Pollution Potential 110
Trends in Groundwater Pollution 112
CONSTITUENTS IN POLLUTED GROUNDWATER 112
Quality Categories 112
Effects of Water Use 112
SOURCES AND CAUSES OF POLLUTION 120
Agricultural Sources and Causes 120
Municipal and Industrial Sources and Causes 124
Groundwater Basin Management 133
Miscellaneous 136
QUALITY IN RELATION TO WATER USE 138
Water Quality Standards 138
Drinking Water 139
Industrial Water 139
Irrigation Water 139
Livestock Water 142

REFERENCES 143

APPENDIX — METRIC CONVERSION TABLE 154

LIST OF FIGURES

Figure No.	Title	Page
1	Boundaries of the Santa Clara-Calleguas groundwater basin, Ventura County, California.	19
2	Relation of groundwater pollution plume size and orientation for a pollution source near a river with different groundwater flow directions.	36
3	Groundwater flow system under idealized homogeneous aquifer conditions.	37
4	Idealized pollution plume configuration for various locations of surface pollution sources.	38
5	Flow lines for steady-state conditions in an aquifer and positions of a pollution front advancing from a percolation pond.	39
6	Water table contours in the vicinity of Stockton, California, Fall 1964.	40
7	Distribution of saline water in a confined aquifer resulting from an oilfield brine disposal pit in southwestern Arkansas.	41
8	Vertical bar graph of chemical quality expressed in milliequivalents per liter.	68
9	Vertical bar graph of chemical quality expressed in milliequivalents per liter which also shows hardness as $CaCO_3$ in milligrams per liter.	69
10	Vertical bar graph of chemical quality expressed in milliequivalents per liter which also shows silica in millimoles per liter.	69
11	Radial vector diagram of chemical quality expressed in milliequivalents per liter.	70
12	Pattern diagram of chemical quality expressed in milliequivalents per liter.	71
13	Circular diagram of chemical quality with subdivisions showing percentages of total milliequivalents per liter.	72

FIGURES (continued)

Figure No.	Title	Page
14	Trilinear diagram of chemical quality expressed in percentages of cations and anions as milliequivalents per liter and represented by two points and a circle.	73
15	Comprehensive trilinear diagram of chemical quality in which five points represent the proportions of cations and anions together with total dissolved solids in milligrams per liter and hardness as $CaCO_3$ in milligrams per liter.	74
16	Variation in chloride concentration with time for groundwater at Burlington, Massachusetts.	75
17	Seasonal variation in nitrate concentration for groundwater at Fresno, California.	76
18	Variation in electrical conductivity of groundwater along the length of the Santa Ana River Basin, California.	78
19	Variation of total dissolved solids with well depth in a portion of the Santa Clara-Calleguas groundwater basin, Ventura County, California.	79
20	Isosalinity map of groundwater in the Santa Clara-Calleguas groundwater basin, Ventura County, California, as of 1966.	80
21	Vertical cross section showing groundwater pollution movement from waste disposal ponds and control by cooling water recharge ponds and purge wells.	81
22	Contours of chloride concentration in groundwater surrounding a brine disposal pit in southwestern Arkansas.	82
23	Plume of groundwater pollution from a landfill near Munich, West Germany, shown by lines of chloride concentration.	83
24	Unconfined and confined aquifers.	86
25	Cumulative curves showing the frequency distribution of various constituents in potable water.	89
26	A hypothetical drainage basin in a humid region showing in plan view the distribution of zones of polluted water in the upper part of the zone of saturation.	93
27	Disposal of household wastes through a conventional septic tank system.	94
28	Diagram showing percolation of pollutants from a disposal pit to a water table aquifer.	95

FIGURES (continued)

Figure No.	Title	Page
29	Diagram showing the horizontal movement of pollutants beneath a disposal pit as a result of clay lenses in the vadose zone above the water table.	96
30	Illustration of a line source of groundwater pollution caused by a leaking sewer.	96
31	Diagram showing pollution of an aquifer by leaching of surface solids.	97
32	Diagram showing how polluted water can be induced to flow from a surface stream to a well.	97
33	Diagram showing floodwater entering a well through an improperly sealed gravel pack.	98
34	Diagram showing movement of pollutants from a recharge well to a nearby pumping well.	99
35	Diagrams showing spread of pollutants injected through wells into water table and artesian aquifers.	100
36	Diagrams showing reversal of aquifer leakage by pumping.	101
37	Diagrams showing aquifer leakage by vertical movement of water through a nonpumping well.	102
38	Diagrams showing lines of flow of pollutants from a recharge pond above a sloping water table.	103
39	Diagram showing migration of saline water caused by lowering of water levels in a gaining stream.	105
40	Plan view of a water table aquifer showing the hypothetical areal extent to which specific pollutants of mixed wastes at a disposal site disperse and move to insignificant levels.	107
41	Types of pollution plumes in the upper part of the zone of saturation (plan view).	107
42	Changes in plumes and factors causing the changes.	109
43	Rating chart for pollution potential in unconfined aquifers of unconsolidated alluvial materials.	111
44	Estimated trend of groundwater pollution in the United States during the 20th century.	113
45	Water quality cycle—sources and uses of water and effects on water quality.	116
46	Agricultural uses of water and their effects on water quality.	117

FIGURES (continued)

Figure No.	Title	Page
47	Industrial uses of water and their effects on water quality.	118
48	Commercial uses of water and their effects on water quality.	119
49	Domestic uses of water and their effects on water quality.	121
50	Schematic vertical cross section through a coastal aquifer showing freshwater and seawater circulations with a transition zone.	134
51	Schematic diagram of upconing of underlying saline water to a pumping well.	135
52	Diagram illustrating the relation of water pollution to impairment for a given water use.	138

LIST OF TABLES

Table No.	Title	Page
1	Major sources and causes of groundwater pollution and methods of waste disposal	21
2	Classification of major potential pollutants in groundwater	26
3	Major sources of groundwater pollution and types of pollutants	26
4	Inorganic chemical pollutants	27
5	Analyses of chemical quality of groundwater presented in tabular form	67
6	Relative abundance of dissolved solids in potable water	88
7	Major natural constituents in groundwater — their sources and effects upon usability	90
8	Classifications of water	92
9	Explanation of plumes shown in Figure 41	108
10	Parameters and constituents which may be included in analyses of groundwater quality	114
11	Principal sources and causes of groundwater pollution	122
12	Normal range of mineral pickup in domestic sewage	127
13	Drinking water standards of the U.S. Public Health Service	140
14	Guide for evaluating the quality of water used for irrigation	141
15	Guide for evaluating the quality of water used by livestock	142

SECTION 1

INTRODUCTION

BACKGROUND AND SCOPE

Groundwater serves as a major source of water supply in the United States. Public water supplies for one-third of the nation's 100 largest cities are derived from groundwater. It is estimated that in rural areas 95 percent of the domestic water and over half of the water for livestock and irrigation are obtained from underground resources. Furthermore, most of the day-to-day base flow of the nation's rivers and streams originates from groundwater discharge.

The natural quality of groundwater tends to be degraded by activities of man. Wastes which are not discharged into lakes, streams or the ocean are deposited on land and from there may migrate downward to pollute groundwater. The extent of this pollution has grown concomitantly in recent decades with increases in population, agriculture, and industry; however, information as to the magnitude of the problem is meager.

Currently, the U. S. Environmental Protection Agency (EPA) has an investigational program of groundwater pollution underway on a regional basis. From the reports already issued (Fuhriman and Barton, 1971; Scalf et al., 1973; van der Leeden et al., 1973, 1975; Miller et al., 1974), it is apparent that there are literally millions of point sources of pollution in existence.

Section I of this report introduces the subject and describes the needs, objectives, and constraints of groundwater quality monitoring, particularly from the viewpoint of the EPA and its given legislative mandates.

Section II presents the monitoring methodology in the form of a series of procedural steps arranged in chronological order. By so doing a straightforward sequence of actions is outlined which can lead to a groundwater quality monitoring program in a given area. To suggest the scope of the monitoring methodology, the 15 steps involved are listed below:

Step 1 — Select Area or Basin for Monitoring

Step 2 — Identify Pollution Sources, Causes, and Methods of Waste Disposal

Step 3 — Identify Potential Pollutants

Step 4 — Define Groundwater Usage

Step 5 — Define Hydrogeologic Situation

Step 6 — Study Existing Groundwater Quality

Step 7 — Evaluate Infiltration Potential for Wastes at the Land Surface

Step 8 — Evaluate Mobility of Pollutants from the Land Surface to the Water Table

Step 9 — Evaluate Attenuation of Pollutants in the Saturated Zone

Step 10 — Prioritize Sources and Causes

Step 11 — Evaluate Existing Monitoring Programs

Step 12 — Establish Alternative Monitoring Approaches

Step 13 — Select and Implement the Monitoring Program

Step 14 — Review and Interpret Monitoring Results

Step 15 — Summarize and Transmit Monitoring Information

The report concludes with a list of references pertaining to groundwater quality and pollution.

It should be noted that this report is one of a series of five reports published by the U.S. Environmental Protection Agency. Although this report is self-contained in the material presented, the other reports provide important supplemental data, information, and examples. The four related reports are briefly described in the following paragraphs.

Monitoring Groundwater Quality: Methods and Costs

This report (Everett et al., 1976) summarizes specific techniques available for monitoring groundwater quality together with detailed estimates, where available, of their costs.

Monitoring Groundwater Quality: Data Management

This report (Hampton, 1976) examines the requirements of a groundwater quality data management information system, reviews existing systems, and identifies how existing capabilities can be utilized for a groundwater quality monitoring program.

Monitoring Groundwater Quality: Economic Framework and Principles

This report (Crouch et al., 1976) reviews the existing institutional and legal structure pertaining to groundwater pollution, presents a hydrogeologic case study as a framework for discussion of economic issues of groundwater monitoring, and analyzes economic principles pertaining to groundwater pollution monitoring.

Monitoring Groundwater Quality: Illustrative Examples

This report (Tinlin, 1976) is designed to show by example selected source-specific and pollutant-specific monitoring procedures. The report first describes five case histories of actual groundwater pollution. The monitoring techniques which were employed in each case are given as well as a retrospective view of these techniques and their efficacy. The report concludes with four illustrative examples for selecting a preferred groundwater pollution monitoring program. These examples are: agricultural return flow, septic tanks, percolation ponds, and solid waste landfills.

In addition to the above reports, the following EPA reports were prepared as a part of this same study and serve as corollary contributions to the monitoring methodology:

EPA-600/4-73-001a (NTIS #PB-232-116/461)	Groundwater Pollution Features of Federal and State Statutes and Regulations, by Fritz van der Leeden (Geraghty & Miller, Inc.), July 1973.
EPA-600/4-73-001b (NTIS #PB-232-117/WP)	Polluted Groundwater: Some Causes, Effects, Controls, and Monitoring, by Harvey O. Banks, Geraghty & Miller, Inc. (James J. Geraghty, David W. Miller, Nathaniel M. Perlmutter, and George R. Wilson), David C. Kleinecke, P.H. McGauhey, Charles F. Meyer (Editor), Richard M. Tinlin, David K. Todd, Edward J. Tschupp, and Don L. Warner, July 1973.
EPA-680/4-74-001 (NTIS #PB-235-556/8WP)	Polluted Groundwater: A Review of the Significant Literature, by David K. Todd and Daniel E. McNulty, March 1974.
EPA-680/4-74-002 (NTIS #PB-241-078)	Polluted Groundwater: Estimating the Effects of Man's Activities, by John F. Karubian, June 1974.
EPA-680/4-74-003 (NTIS #PB-241-402)	Rationale and Methodology for Monitoring Groundwater Polluted by Mining Activities, by Don L. Warner, June 1974.
EPA-680/4-75-008	Monitoring Disposal-Well Systems, by Don L. Warner, July 1975.

PURPOSE AND APPROACH

The monitoring methodology described in this report is intended to serve as a set of guidelines for developing and implementing a groundwater quality monitoring program. It should be apparent that factors such as climate, hydrology, population, pollution sources, and water use vary from place to place; therefore, the design of an appropriate monitoring program will also vary accordingly. No one set of guidelines can cover all situations; however, with judgment the approach presented herein can be extended and interpreted to meet most other situations which will be confronted in the field.

The physical, chemical, and biological mechanisms governing groundwater pollution are reasonably well understood. Yet, applying this knowledge to the many different situations which can result from superimposing a given groundwater pollution source upon particular hydrogeologic environments is difficult. Nonetheless, this report is intended to be a handbook or manual for the development and implementation of a methodology for monitoring groundwater quality. The methodology is expressed in a generalized form so that it can be usefully employed by regional, State, and local water pollution control agencies and is applicable to all types of groundwater aquifers, areas, and basins. Alternatives in the decision-making process leading to the final monitoring program are considered throughout the methodology.

Monitoring may be defined as a scientifically designed surveillance system of continuing measurements and observations, including evaluation procedures. The EPA is currently involved in establishing, in cooperation with the States, a national groundwater quality monitoring system as part of its legislatively directed program to prevent, reduce, and eliminate groundwater pollution.

Four basic types of monitoring have been defined by the EPA. In terms of groundwater quality, these may be interpreted as follows:

Ambient Trend Monitoring

This concerns measurements of groundwater quality and deviations in relation to standards, and involves temporal and spatial trends within a groundwater basin or area.

Source Monitoring

This involves the measurement of effluent quantity and quality for pollution sources which may affect groundwater.

Case Preparation Monitoring

This serves to gather evidence for enforcement actions of past, existing or anticipated groundwater pollution situations; implied are carefully documented measurements within a circumscribed area.

Research Monitoring

This contributes to research investigations on groundwater quality and pollution occurrence and movement.

Of the four above types, the monitoring methodology is directed largely toward source monitoring. Case preparation and research monitoring, while providing valuable data, are clearly specialized needs which do not lend themselves to a national program. Ambient trend monitoring provides background quality information on groundwater resources (such as the ongoing programs of the U.S. Geological Survey). Thus, a national program to protect groundwater quality relative to those activities of man which pollute groundwater will focus primarily on measurements relating to pollution sources and methods of waste disposal which contribute to pollution. Furthermore, because it is infeasible to monitor all sources and causes of pollution, the methodology concentrates on identifying the most important sources and methods of disposal. In essence then the methodology becomes a resource allocation problem with the goal of developing a cost-effective monitoring program which will contribute most to the protection of the nation's groundwaters.

NEEDS AND OBJECTIVES

Growing evidence indicates that the nation's groundwaters (like its other resources such as air and surface water) are becoming excessively polluted. Groundwaters are not being efficiently allocated among their alternative uses. Wastes are an unavoidable byproduct of all man's activities and, recognizing that, these wastes must be disposed of somewhere. The substantive questions of optimum production of wastes and their optimum disposal must be addressed. Clearly, the nation's aquifers, like every other sector of the environment, must serve as a repository for the disposal of some of society's wastes. The question, then, is not "can wastes be placed on and in the ground?" but rather "where and how much?"

Economic Needs and Objectives

In order to maximize the value of groundwater resources from society's point of view, it is necessary that they be used in optimal amounts for various appropriate purposes such as irrigation, cooling, drinking, etc, as well as for the disposal of wastes.

The reason that groundwaters become excessively polluted is exactly the same as the reason that our other environmental resources become excessively polluted; namely, the fact that well-specified (and, therefore, easily enforceable) property rights do not exist in the resource. As Corker's (1971) authoritative legal analysis makes abundantly clear, property rights in groundwater are very poorly specified. As a result, some parties use other parties' groundwater resources without authorization as a receptor for their wastes, thereby imposing uncompensated damages on the resource owner. In the absence of any obligation to compensate parties whose groundwater is serving as a waste disposal site, such waste disposal service appears to be free to the polluter (although it is obviously not free from society's point of view). In such a situation, the polluter will utilize such a service until the marginal private benefit he obtains by using that service is driven down to zero, even though the marginal social cost may be positive and large. Consequently, the aquifer's waste receptor capabilities are abused, and groundwater becomes excessively polluted.

When well-specified property rights to a resource do not exist, the market processes through which our resources are normally allocated break down as an efficient resource allocation mechanism. Therefore, if resources to which well-specified property rights do not exist are to be efficiently allocated among their alternative uses, it is not possible to rely on the normal allocation mechanism provided by market processes. The resource must, instead, be managed by some public agency.

As pointed out by the U.S. Council on Environmental Quality (1973, Chapter 3), efficient management of our environmental resources requires that consideration be given to four categories of costs. First, there are damage costs. These are costs which are generated directly by a polluting activity. With respect to groundwater resources, one example would be increased physiological damage caused by pollution of drinking water. Another example would be crop losses resulting from salt buildup in an irrigation well. Second, there are avoidance costs. These are costs which are incurred by society in order to avoid, or reduce, damage costs. With respect to groundwater resources, one example would be the importation of unpolluted water to replace that previously obtained from a well that has become polluted. Third, there are abatement costs. These are costs associated with the reduction of pollution. Such reduction of pollution can be achieved either by controlling the source or by treating the polluted water. With respect to groundwater resources, one example would be the deep injection into a safe geologic zone of noxious effluents previously disposed of at the land surface, into the atmosphere, surface waters, or landfill. Fourth, there are transaction costs. Transaction costs include the cost of resources allocated to the establishment, and of enforcement of environment-preserving policies and regulations. With respect to groundwater resources, the most important example of a transaction cost, and of special relevance to this study, would be the cost of monitoring groundwater pollution either to generate information on quantity and quality or to detect violations of, and ensure compliance with, groundwater quality standards.

The essential principle to note is that these four cost categories are, in general, interdependent. Thus, any new groundwater quality policy will probably affect all four categories. For example, if a policy is introduced which is designed to reduce groundwater pollution, it will certainly reduce damage costs but may very well increase abatement, avoidance, and monitoring costs. Usually, each feasible groundwater quality policy will affect these four categories of cost differently. Obviously the only groundwater quality policy alternative that should be seriously considered for implementation is that set of policies for which the reduction in damage costs exceeds the net increase, if any, in avoidance, abatement, and monitoring costs. To go even further than this, the most efficient, or optimal, groundwater quality policy among the feasible set of alternatives is that policy which minimizes the sum of the damage costs, avoidance costs, abatement costs, and monitoring costs for a given groundwater pollution situation. Implicitly, the minimization of these costs is equivalent to the maximization of society's income or gross national product.

To illustrate by example, sewer leakage is known to pollute groundwater and may, therefore, impose certain damage costs and avoidance costs. However, with present technology there is no way of controlling this source of pollution that does not impose abatement costs that are far in excess of the reduction in damage and avoidance costs which would be achieved. It follows that the efficient policy is not to monitor and abate this pollution source, but simply to accept the existing level of damage and avoidance costs.

Of course, in many other groundwater pollution situations the reduction in damage costs will exceed the increase in avoidance, abatement, and monitoring costs that bring these reductions about. The objective then becomes that of selecting the avoidance, abatement, and monitoring strategy which generates, at the margin, decreases in damage costs just equal to the increases in the avoidance, abatement, and monitoring costs required by the strategy.

The attainment of this objective will not simply involve the minimization of monitoring costs by the responsible government agency. For example, in any given groundwater pollution situation there may well be several different abatement strategies, each with an associated monitoring requirement, that would achieve the desired level of groundwater quality. If the public agency responsible for selecting among the abatement and monitoring strategies simply chooses that alternative which minimizes its own monitoring costs, this could imply higher private abatement costs with the result that the combined monitoring and abatement costs of that policy would be greater than the combined monitoring and abatement costs of some other strategy. Clearly, this would not be efficient from society's point of view.

EPA Needs and Objectives

The needs and objectives of the EPA for those data pertaining to groundwater quality which must be obtained through monitoring programs, are dictated by the mandates and requirements of the Federal Water Pollution Control Act, as amended (Public Law 92-500; 33 USC 1151, et seq.), and the Safe Drinking Water Act (Public Law 93-523; 42 USC 300f, et seq.).

FEDERAL WATER POLLUTION ACT, AS AMENDED. The objective of the Act as amended as stated in Sec. 101 (a) is:

> Sec. 101. (a) The objective of this Act is to restore and maintain the chemical, physical, and biological integrity of the Nation's waters...

The definition of "pollution" given in the Act indicates clearly the wide spectrum of groundwater quality problems and of the sources and causes of those problems that may need to be considered in designing a groundwater quality monitoring program:

> Sec. 502. (19) The term 'pollution' means the man-made or man-induced alteration of the chemical, physical, biological, and radiological integrity of water.

The Act directs that specific programs be developed to improve and maintain groundwater quality:

> Sec. 102. (a) The Administrator (of EPA) shall, after careful investigation, and in cooperation with other Federal agencies, State water pollution control agencies, interstate agencies, and the municipalities and industries involved, prepare or develop comprehensive programs for preventing, reducing, or eliminating the pollution of the navigable waters and ground waters and improving the sanitary condition of surface and underground waters. In the development of such comprehensive programs due regard shall be given to the improvements which are necessary to conserve such waters for the protection and propagation of fish and aquatic life and wildlife, recreational purposes, and the withdrawal of such waters for public water supply, agricultural, industrial, and other purposes. For the purpose of this section, the Administrator is authorized to make joint investigations with any such agencies of the condition of any waters in any State or States, and of the discharges of any sewage,

> industrial wastes, or substances which may adversely affect such waters. [Emphasis added]

Development of cost-effective programs to accomplish this purpose requires an adequate data base that can only be obtained by carefully designed and implemented monitoring programs.

Establishment and conduct of monitoring programs is mandated by the Act:

> Sec. 104. (a) The Administrator (of EPA) shall establish national programs for the prevention, reduction, and elimination of pollution and as part of such programs shall: ...
>
> > (5) in cooperation with the States, and their political subdivisions, and other Federal agencies establish, equip, and maintain a water quality surveillance system for the purpose of monitoring the quality of the navigable waters and ground waters and the contiguous zone and the oceans...and shall report on such quality... [Emphasis and insertion added]
>
> Sec. 106. (e) Beginning in fiscal year 1974 the Administrator shall not make any grant under this section (Sec. 106) to any State which has not provided or is not carrying out as a part of its program...
>
> > (1) the establishment and operation of appropriate devices, methods, systems, and procedures necessary to monitor, and to compile and analyze data on (including classification according to eutrophic condition), the quality of navigable waters and to the extent practicable, ground waters including biological monitoring; and provision for annually updating such data and including it in the report required under section 305 of this Act; ... [Emphasis and insertion added]

SAFE DRINKING WATER ACT. This Act, which became effective 16 December 1974, places additional responsbilities of major public health and economic significance upon the Administrator of the EPA to protect the nation's groundwater resources. The following excerpts from the Act indicate the nature and extent of those responsibilities:

> Sec. 1424. (e) If the Administrator (of EPA) determines, on his own initiative or upon petition, that an area has an aquifer which is the sole or principal drinking water source for the area and which, if contaminated, would create a significant hazard to public health, he shall publish notice of that determination

> in the Federal Register. *After the publication of any such notice, no commitment for Federal financial assistance* (through a grant, contract, loan guarantee, or otherwise) *may be entered into for any project which the Administrator determines may contaminate such aquifer through a recharge zone* so as to create a significant hazard to public health, but a commitment for Federal financial assistance may, if authorized under another provision of law, be entered into to plan or design the project to assure that it will not, so contaminate the aquifer. [Emphasis and insertion added]
>
> Sec. 1442. (a)(1) The Administrator may conduct research, studies, and demonstrations relating...to the provision of a dependably safe supply of drinking water, including...
>
>> (E) *improved methods of protecting underground water sources* of public water systems *from contamination*...
>>
>> Sec. 1442. (a)(4) The Administrator shall conduct a survey and study of...
>>
>> (A) *disposal of waste* (including residential waste) *which may endanger* underground water which supplies, or can reasonably be expected to supply, any public water systems, and
>>
>> (B) means of control of such waste disposal...
>>
>> Sec. 1442. (a)(5) The Administrator shall carry out a study of methods of underground injection which do not result in the degradation of underground drinking water sources.
>>
>> (6) The Administrator shall carry out a study of methods of preventing, detecting, and dealing with *surface spills of contaminants* which may *degrade underground water sources* for public water systems...
>>
>> (8) The Administrator shall carry out a study of the *nature and extent of the impact on underground water* which supplies or can reasonably be expected to supply public water systems of (A) *abandoned injection or extraction wells*; (B) intensive *application of pesticides and fertilizers* in underground water recharge areas; and (C) *ponds, pools, lagoons, pits, or other surface disposal of contaminants* in underground water recharge areas. [Emphasis added]

To carry out these responsibilities effectively, detailed information for many aquifers on groundwater quality, geology, hydrology and the sources and causes of groundwater quality impairment, will be necessary. Groundwater quality monitoring programs must be designed to provide such data where and when required.

INTERSTATE COMPACTS. A few interstate compacts – the Federal-interstate compacts for the Delaware River Basin and the Susquehanna River Basin are examples – provide authority for the compact commissions to monitor groundwater quality and to develop and implement plans for quality protection.

STATE STATUTES AND REGULATIONS. State laws and implementing regulations vary widely from State to State as regards both groundwater quality monitoring and the development and implementation of plans for quality protection. In California, the State Water Resources Control Board and the nine regional water quality control boards have broad authority and responsibilities in this regard under Division 7 of the Water Code (Porter-Cologne Water Quality Control Act, as amended). Likewise, the Water Code provides with respect to the State Department of Water Resources:

> 229. (Water Code) The Department of Water Resources, either independently or in cooperation with any person or any county, State, Federal, or other agency, to the extent that funds are allocated therefore, *shall investigate conditions of the quality of all waters* (including ground waters) within the State, including saline waters, coastal and inland, as related to *all sources of pollution of whatever nature* and shall report thereon to the Legislature, to the board (State Water Resources Control Board), and to the appropriate regional water quality control board annually, and *may recommend any steps which might be taken to improve or protect the quality of such waters.* The department shall coordinate its investigations fully with the board. [Emphasis and insertions added]

The Water Code of the State of Texas provides similar authorities and responsibilities to the Texas Water Quality Board, and, to some extent, to the Texas Water Development Board.

Some States have not yet progressed as far in monitoring and planning for the improvement and protection of groundwater quality.

Monitoring Objectives

Simply stated, the objective of a monitoring program should be to collect, manage, and analyze the data on groundwater quality and the sources and causes of groundwater pollution, and the other information – geologic, hydrologic, and economic – necessary to enable the EPA and the State(s) involved to fulfill their statutory responsibilities as regards protection of groundwater quality, that is "...to restore and maintain the chemical, physical, and biological integrity of the nation's waters..."

To fulfill that objective, a specific monitoring program must be developed and implemented for each groundwater basin; such a program will be the end result of the application of the monitoring methodology described in this report. The data to be obtained may be needed for one or more of the following purposes, depending upon the types, extent, and seriousness of quality problems, and the present and future importance of the groundwater system as a source of water supply:

- Provision of background information and quality
- Detection of quality trends
- Identification and assessment of the sources and causes of pollution
- Planning — including formulation, calibration, verification, and use of planning models
- Establishment of water quality standards and effluent limitations
- Formulation of other regulatory control and management actions necessary to protect quality
- Compliance
- Enforcement
- Reporting.

For a groundwater basin which is already extensively developed, or in process of development, all these purposes must generally be served, although the relative emphasis will vary.

A wide range of types of data may be needed, depending upon the particular groundwater system involved, its importance, uses, its present and potential quality problems, and the information already available. In addition to water quality data this information should include:

- Geologic characteristics
- Hydrology
- Hydraulic characteristics
- Land use
- Water resource development and use

- Demographic and economic conditions
- Waste generation and disposal.

An effective monitoring program must recognize the dynamic nature of groundwater systems as affected by both natural phenomena and man-induced changes. The program must, therefore, be continuing. Its scope and relative emphasis will change over time. The data obtained must be adequate to enable prediction of potential quality problems and for formulation of plans for prevention of groundwater pollution.

CONSTRAINTS

There are several constraints to be considered in the design of a cost-effective monitoring program — institutional, budgetary, legal, social, and personnel.

At the Federal level, there are several agencies in addition to the EPA and USGS which collect groundwater quality data and which possess information of value to a comprehensive groundwater quality monitoring program. Their monitoring activities are accomplished in support of their statutorily authorized programs which involve groundwater and its uses in some manner. Other programs of particular significance are those of U. S. Bureau of Reclamation, U. S. Army Corps of Engineers, and U. S. Soil Conservation Service.

There are several State agencies which have statutorily defined authorities and responsibilities with respect to groundwater, and which conduct monitoring activities. Such State entities may include:

- Water resource planning and management agencies
- Water quality control agencies
- Water rights administration
- Department of public health
- Universities
- Soil conservation agencies.

The authorities, responsibilities, and activities of the several State agencies may overlap to some extent.

At the regional and local levels of government, counties, municipalities, and special political jurisdictions such as water supply, sanitary, flood control, and water conservation districts, have interests and responsibilities with respect to groundwater, and many conduct extensive monitoring programs.

The authorities, responsibilities, and programs of the several agencies at each governmental level and the data already available from their monitoring activities must be taken into account in designing a new monitoring system.

The number of geologists, hydrologists, and water quality specialists competent to design and implement a groundwater quality monitoring program and to make effective use of the data generated is limited.

Funds available for monitoring activities are generally scarce, particularly at the State, regional, and local levels of government. Any increase in budgets will take place gradually and then only on well-documented justification. As a consequence, the implementation of expanded monitoring programs must, in general, take place gradually.

SECTION II

MONITORING METHODOLOGY

CONCEPT OF A MONITORING METHODOLOGY

The basic purpose of a methodology for monitoring groundwater pollution is to provide a framework for the planning and development of a monitoring program. The methodology should serve two roles simultaneously. First, it should assist a local designated monitoring agency (DMA) to design and to implement a monitoring program. The second role should be to guide governmental agencies at the State and national levels in establishing realistic monitoring priorities, not only in terms of what should be monitored and where, but also in terms of timing and funding.

The monitoring methodology described in the following sections is predicated upon the technical effort being organized and conducted by or under the direct supervision of personnel with professional training in water resources engineering or groundwater geology. This requirement is essential in view of the fact that it is infeasible to summarize the full background of hydrogeology, involving the occurrence, distribution, and movement of groundwater, as well as its geochemistry, which would be needed to establish a successful monitoring program. Section III of this report has been prepared specifically for hydrologists and geologists not familiar with groundwater quality problems. It is recommended that these individuals review Section III prior to using this section.

Various personnel arrangements can be anticipated for implementing the monitoring methodology. Indicative of the possibilities are the three following situations:

- In an urbanized local area the DMA might possess a sufficiently large technical staff so that the organization and conduct of the monitoring program could be handled entirely by this in-house group. Similarly, for a relatively undeveloped area where the monitoring program would be small, a single technically competent member of the DMA might personally supervise the program.
- Where the staff of a DMA is inadequate, responsibility for the monitoring program could be subcontracted to a firm of consulting engineers or geologists specializing in groundwater.

An arrangement of this sort could function either on a continuing basis or until an adequate in-house staff became available.

- With the passage of time and the full development of a monitoring program, surveillance of existing and potential sources of pollution will assume a standardized routine. Thereafter, attention will tend to be focused primarily on the monitoring of new developments, such as landfills, feedlots, industrial plants, subdivisions, etc. Because plans for each new development will need to be reviewed and approved by the DMA, it follows that inclusion of an adequate monitoring system will become a contingency for approval. Under these circumstances much of the work required to extend the monitoring program for these new developments will be completed by the engineering firms responsible for their design.

Finally, it should be understood that the methodology presented herein must of necessity be somewhat generalized. There is an infinite number of combinations of pollution causes, hydrogeologic situations, and monitoring methods, among other variables, that can govern the implementation of a monitoring program. Therefore, persons involved in a monitoring program will be required to exercise professional judgment in order to interpret and to apply this methodology to the specific local situations which they encounter. Examples are given for illustrative purposes and case histories are presented by Tinlin (1976).

IMPLEMENTATION OF A MONITORING METHODOLOGY

The following material describes procedures for implementing a groundwater pollution monitoring program. These apply to a specified local area under the jurisdiction of a DMA. The procedures are described as a series of steps arranged in chronological order. In practice, however, activities of different steps will overlap in order to make efficient use of personnel and time.

The steps constitute a series of monitoring objectives for a DMA. Taken together they constitute a monitoring methodology which can assist a DMA at any location in the United States to initiate its groundwater pollution monitoring program.

Step 1 — Select Area or Basin for Monitoring

The selection of areas to be monitored will be made within a State by the appropriate State water pollution control agency that, in cooperation with the EPA, carries out the mandates of PL 92-500 and PL 93-523. The basis for selecting areas will be governed, in general, by a combination of administrative, physiographic, and priority considerations. Each of these factors will be reviewed in the following paragraphs.

ADMINISTRATIVE CONSIDERATIONS. The initiation of a monitoring program requires that a local DMA be specified. In many situations the requisite agency with the necessary technical staff may be a county, district, or regional water organization. Thus, the area to be monitored can often be made to correspond to the jurisdictional area of the DMA. The size of a particular area may vary from a few square miles to thousands of square miles.* Size alone is less important than the ready accessibility of all portions of the area to the DMA as well as hydrogeologic knowledge of the area possessed by the DMA.

It should be recognized that political boundaries frequently create problems in terms of water management. Such a boundary may cross a major groundwater basin so that, for example, pollutants from an adjoining area may be entering from sources not subject to monitoring by the DMA. Clearly, such situations should be minimized as much as possible; alternatively, cooperation among DMA's sharing common groundwater pollution problems will be essential to the success of their respective monitoring programs.

PHYSIOGRAPHIC CONSIDERATIONS. The physiographic basis for selecting monitoring areas recognizes that groundwater basins are distinct hydrographic units containing one or more aquifers. Such basins usually, but not always, coincide with surface water drainage basins. By establishing a monitoring area related to a groundwater basin, total hydrologic inflows to and outflows from the basin are fully encompassed. This permits all pollution sources and their consequent effects on groundwater quality to be monitored by a single DMA. Where basins are extensive, monitoring areas become too large to be practical. Boundaries should then be drawn parallel to groundwater flows or where cross-flow components are insignificant. Most groundwater basins in the United States have been mapped, based on hydrogeologic investigations, and information is available from State water agencies and/or the U.S. Geological Survey.

PRIORITY CONSIDERATIONS. It is recognized that establishment of a national program to assess the impact of man's activities on groundwater quality will develop gradually because of administrative, budgetary, and personnel constraints. Since it is the stated intent of the EPA to rely on the States to select the areas to be monitored and to conduct the appropriate monitoring activities, any national program which evolves will as a consequence be built upon the data and information generated by these State monitoring activities.

A first consideration of a State will be to select and prioritize those groundwater aquifers subject to the greatest pollution threat. This first level of prioritization is necessary to provide a starting point for application of the groundwater monitoring methodology. Rarely will sufficient data and information be available from the start to make anything but a gross appraisal of the threat to a State's groundwater resources.

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*See Appendix for conversion to metric units.

In order for the application of the methodology to be most effective on a spatial basis, areas which have the largest number of identified or potential pollution sources and where there is a high utilization of groundwater should be ranked and sectioned off as areas within which to apply the monitoring methodology. By utilizing the above two criteria in combination with the administrative and physiographic considerations previously set forth, the total area of a State can be divided into areas which may require a monitoring program.

Illustrative of this procedure is an expanded priority scheme for groundwater monitoring developed by the State of California. Here groundwater basins are ranked according to the following five criteria.

- Basin population
- Agricultural use of groundwater
- Estimated usable groundwater capacity
- Availability of an alternate water supply source
- Number of existing quality problems which threaten the groundwater resource.

This list essentially restates the two criteria described above but attempts to add further insight into water resource management rather than a groundwater pollution monitoring program. This approach developed in California is cited as an example only and is not necessarily recommended by the EPA.

In summary, the administrative, physiographic, and priority considerations provide a rationale for selecting monitoring areas. To be applied within a given State they must be interpreted as guidelines because various special or local conditions will frequently have to be accommodated. Compromises will be inevitable, but careful initial selection of monitoring areas can simplify and make more effective the subsequent monitoring program undertaken by each DMA.

EXAMPLE – BASIN BOUNDARY AREA. Figure 1 shows the boundaries selected for defining the groundwater basin in the Santa Clara-Calleguas area in southwestern Ventura County, California. The northern and southern boundaries were placed along mountain ridges where groundwater flow would be either nonexistent or parallel to the boundary. The eastern boundary was drawn at the county line, a political boundary, but here this also coincides closely with the drainage divide of the stream systems. The western boundary was the seacoast. The predominant groundwater flow is in a southwesterly, or down-valley, direction toward the sea except locally

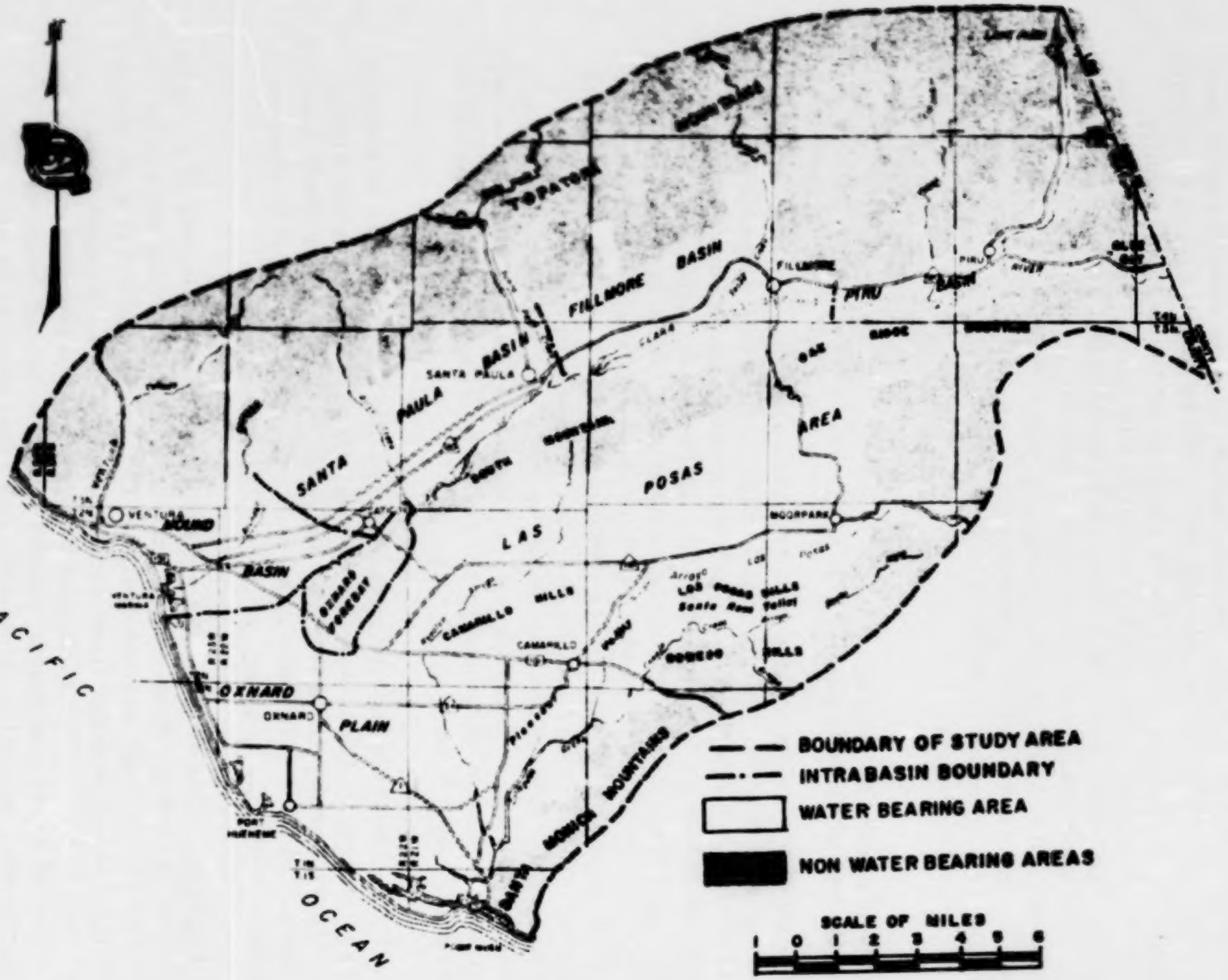

TOPATOPA
MOUNTAINS
FILLMORE BASIN
SANTA PAULA BASIN
SANTA PAULA
FILLMORE
PIRU BASIN
PIRU
OAK RIDGE
SANTA CLARA
SOUTH MOUNTAIN
LAS POSAS AREA
MOORPARK
VENTURA
MOUND BASIN
OXNARD
OXNARD PLAIN
PORT HUENEME
CAMARILLO
CAMARILLO HILLS
LAS POSAS HILLS
Santa Rosa Valley
CONEJO HILLS
SANTA MONICA MOUNTAINS
PACIFIC
OCEAN
BOUNDARY OF STUDY AREA
INTRABASIN BOUNDARY
WATER BEARING AREA
NON WATER BEARING AREAS
SCALE OF MILES
1 0 1 2 3 4 5 6

Figure 1. Boundaries of the Santa Clara–Calleguas groundwater basin, Ventura County, California (California Department of Water Resources, December 1974).

where major pumping centers cause deviations or reversals of the flow direction.

It should be noted in Figure 1 that the water-bearing area occupies some 192,000 acres and that this is only a fraction of the total area, hence monitoring would be restricted to only those portions of the area containing groundwater. Six population centers lie within the area (Ventura, Oxnard, Santa Paula, Fillmore, Piru, and Moorpark) with a total 1970 population of 330,000. The aquifers are all composed of alluvial materials with unconfined, confined, and multiple types being present. The area of urban land use totals 27,000 acres, while agricultural use covers 106,000 acres. Average annual precipitation is 15.05 inches, which occurs chiefly in winter from North Pacific storms.

Step 2 — Identify Pollution Sources, Causes and Methods of Waste Disposal

The design of a monitoring program requires that the potential sources and causes of groundwater pollution and methods of waste disposal within an area be identified. Groundwater pollution sources can be conveniently placed into six major groups. Municipal, agricultural, and industrial are three major groups. For purposes of monitoring groundwater pollution, oil-field wastes and mining wastes are considered of sufficient importance to also be listed as major groups. The remaining sources are grouped under miscellaneous. Of considerable importance to monitoring efforts is the identification of the type of source, as to whether it is a point, line, or diffuse, source. Several sources have more than one primary disposal method. Table 1 summarizes the sources and causes of pollution, and common methods of waste disposal, where applicable.

MUNICIPAL. Three urban groundwater pollution sources are associated with sewage: sewer leakage, sewage effluent disposal, and sewage sludge disposal. Urban runoff, solid wastes, and lawn fertilizers are other sources of importance. Since septic tanks also occur in rural areas, they are discussed under a separate heading.

Sewer Leakage. One of the more recently recognized sources of groundwater pollution is leakage from sewer lines. Most monitoring programs for detection of sewer leakage are not designed for groundwater pollution evaluations. In the case of leakage from deep sewers, all of the topsoil and a significant part of the vadose zone may be bypassed. Information on the location of sewered areas and major sewers can be obtained from local public works departments, sanitation districts, and regulatory agencies. Pertinent information on the sizes of major sewers, type of pipe and joints, age, pressurization, and leaks should be compiled.

TABLE 1. MAJOR SOURCES AND CAUSES OF GROUNDWATER POLLUTION AND METHODS OF WASTE DISPOSAL

SOURCE	CATEGORY			COMMON METHOD OF DISPOSAL						
	Point	Line	Diffuse	Percolation Pond	Surface Spreading and Irrigation	Seepage Pits and Trenches	Dry Stream Beds	Landfills	Disposal Wells	Injection Wells
Municipal										
Sewer Leakage	X	X		NOT APPLICABLE						
Sewage Effluent	X	X	X	X	X		X		X	
Sewage Sludge	X		X		X	X		X		
Urban Runoff	X	X	X	X	X		X		X	
Solid Wastes	X				X			X		
Lawn Fertilizers			X		X					
Agricultural										
Evapotranspiration and Leaching (Return Flow)			X		X					
Fertilizers			X		X					
Soil Amendments			X		X					
Pesticides and Herbicides			X		X					
Animal Wastes (Feedlots and Dairies)	X		X	X	X	X		X		
Stockpiles	X			NOT APPLICABLE						
Industrial										
Cooling Water	X		X	X					X	
Process Waters	X			X					X	X
Storm Runoff	X		X	X	X		X		X	
Boiler Blowdown	X			X					X	
Stockpiles	X			NOT APPLICABLE						
Water Treatment Plant Effluent	X			X				X	X	
Hydrocarbons	X			X					X	X
Tanks and Pipeline Leaks	X	X		NOT APPLICABLE						
Oilfield Wastes										
Brines	X	X	X	X	X	X	X			X
Hydrocarbons	X			X					X	X
Mining Wastes	X	X	X	X			X	X	X	X
Miscellaneous										
Polluted Precipitation and Surface Water		X	X	NOT APPLICABLE						
Septic Tanks and Cesspools			X		X	X		X		
Highway Deicing		X		NOT APPLICABLE						
Seawater Intrusion			X	NOT APPLICABLE						

Sewage Effluent. Sewage effluent has commonly been disposed of to groundwater by a number of methods. Crop and forest irrigation, percolation basins, dry stream beds, and disposal wells have been commonly used for disposal of sewage effluent. Information on the location of treatment and disposal facilities, methods of treatment and disposal, and effluent volumes can be obtained from local public works departments, sanitation districts, and regulatory agencies. Percolation basins and dry stream beds used for disposal can be commonly seen on aerial photographs and crop surveys may indicate lands where sewage effluent is used for irrigation.

Sewage Sludge. Sewage sludge is often allowed to dry in open basins from which percolation may occur. Also, the dried sludge is commonly applied to agricultural lands as fertilizer. Information on the weight of sludge production and method of disposal can be obtained from local public works departments and sanitation districts. Sludge drying beds may be located from aerial photographs.

Urban Runoff. Precipitation falling on paved and other impermeable areas can pick up significant pollutant loads. Much storm water runoff is now being collected, treated, and disposed of separately from sewage. Common methods of disposal include percolation ponds, dry stream channels, disposal wells, and irrigation. Information on treatment and disposal methods and volumes of waste water can be obtained from local flood control districts, public works departments, and regulatory agencies.

Solid Wastes. Locations of municipal solid waste disposal sites can be obtained from public works departments, local sanitary districts, and regulatory agencies. Regional solid waste planning documents may also be available. The type of site (sanitary landfill or refuse dump), the type of wastes, the annual volume or weight, and the provisions for control of leachate should be determined.

Lawn Fertilizers. Applications of water and fertilizer in amounts greater than that used by plants in urban areas can produce groundwater pollution. Information on types of fertilizers and amounts is difficult to obtain, because of the diversity of practice from one household to the next. Fertilizer consumption may be estimated from sales records by manufacturers or retailers. Information on irrigation rates would be important but are usually not available.

AGRICULTURAL.

Evapotranspiration and Leaching. The process of irrigation of agricultural lands generally results in some water percolating past the root zone. This percolating water is usually degraded with respect to the applied water due to concentration by evapotranspiration, dissolution of mineral matter in the soil, and additives that are applied at the land surface. Fertilizers, soil amendments, and pesticides are considered separately in this section due to their importance in groundwater pollution. Irrigated lands can be identified from aerial photographs or crop surveys, available from the USDA Agricultural Research Service, farm advisors, or irrigation districts. Data on the quality of return flow is rarely available. However, estimates can be made based on the water application rates and consumptive use. The volume of return flow can be calculated from records of precipitation, applied water, and evapotranspiration.

Records of applied water volumes may be obtained from irrigation districts, farmers, power companies, and governmental agencies concerned with water delivery. The calculation of return flow volumes is more fully discussed in Step 7 of this report.

Fertilizers. Fertilizers in modern agriculture are applied to almost all crops, whether irrigated or not. Fertilizer application rates usually vary with crop type, soil conditions, and irrigation practice. Local farm advisors can provide information on types and amounts of fertilizers applied. Records of fertilizer sales from manufacturers or retailers can be used to estimate application rates. Regulatory agencies may also have data on fertilizer use.

Soil Amendments. Soil amendments are applied to irrigated lands to alter the physical or chemical properties of the soil. Acid soils may be treated with lime to raise the pH, thus creating more favorable growing conditions for plants. Gypsum or sulfur is widely used to increase infiltration rates on some soils. Irrigation waters in which sodium is the predominant cation may produce dispersion of the soil structure and result in low infiltration rates. The calcium in the applied gypsum replaces sodium in the soil and counteracts this soil clogging. Substantial amounts of these soil amendments may eventually be leached into the groundwater, thereby increasing its salinity. Records of application rates may be obtained from farm advisors and manufacturers.

Pesticides and Herbicides. Pesticides may be significant in agricultural areas as a diffuse source of groundwater pollution. Pesticides, insecticides, herbicides, fungicides, and other chemicals are used to control nuisance organisms. Although many pesticides can be retained in the soil or degraded, some have been found to be readily leached into the groundwater. Farm advisors may have information on the types of pesticides used and application rates. Manufacturers, retailers, and regulatory agencies may have records on amounts sold in certain areas.

Animal Wastes. Livestock wastes generally constitute a minor groundwater pollution source, except where large numbers of animals are confined within small areas. This situation is usually limited to feedlots and dairies. Dairies present additional problems related to the disposal of wash water.

Animal waste disposal by percolation ponds and crop irrigation is common. Feedlots and dairies can be located from land-use maps, zoning maps, and aerial photographs. Information on the number of animals, annual weight of solid waste, and volume of liquid waste can be obtained from farm advisors, dairy and feedlot operators, cattle and dairy associations, and regulatory agencies.

Stockpiles. Unprotected stockpiles in agricultural areas may result in groundwater pollution, particularly where substantial leaching into the soil occurs. These stockpiles include manure; solid chemicals, such as gypsum or sulfur; and miscellaneous waste solids and liquids, such as pesticide containers. Field surveys are often necessary to detect such occurrences.

INDUSTRIAL. Industrial waste flows are usually related to the amount of raw material processed, to the amount of finished product, or to the number of people employed in the factory. Data on industrial waste flows can be obtained from local industries and regulatory agencies. Stockpiles and percolation ponds can be seen on aerial photographs. Data on injection wells have been compiled by the U. S. Geological Survey.

OILFIELD WASTES. Brines are commonly withdrawn from the ground during oil and natural gas production and must subsequently be discarded. Disposal of brines in percolation ponds and injection wells has been widespread. Brines may also be disposed of in dry stream beds, while some brines of low salinity may be used for crop irrigation. Hydrocarbons may be another source of groundwater pollution where wastes are confined in ponds at the land surface. Improperly constructed producing or injection wells can cause significant groundwater pollution. Information on quantity and type of wastes is often available from State oil and gas commissions, regulatory agencies, and local operators.

MINING WASTES. The mining and milling of coal and metallic ores, whether from surface or underground mines, can cause groundwater pollution; therefore, these installations need to be clearly identified if they occur in a monitoring area. Information on mines, their types, their depth, their areal extent, and the amounts and composition of wastes produced is usually available from a State mining agency, the U. S. Bureau of Mines, mining companies, and regulatory agencies.

MISCELLANEOUS.

Polluted Precipitation and Surface Water. Precipitation can be polluted from municipal sources, such as industries and automobile exhaust, as well as agricultural activities, such as the application of ammonia fertilizers. In humid areas, where rainfall is readily leached into the groundwater, pollutants from precipitation may reach the water table. In arid areas, the pollutants in precipitation may accumulate on the land surface and subsequently be leached by irrigation water. Areas where infiltration and percolation to the groundwater may occur from polluted surface water should be identified. Infiltration and percolation rates may be available from hydrogeologic studies by the U. S. Geological Survey, State geological or water agencies, or others.

Septic Tanks and Cesspools. In unsewered areas large numbers of septic tanks and cesspools may be found. Although each is a point source with respect to an individual lot, over large areas septic tanks are diffuse sources of groundwater pollution. Methods of disposal commonly include seepage pits, seepage trenches, and occasionally disposal wells. Location densities, and estimated volume of effluent can be obtained from zoning maps, public works departments, sanitation districts, and regulatory agencies.

Highway Deicing. Sodium chloride and calcium chloride salts are commonly applied to roads to inhibit or to remove ice. Information on the application of salts for deicing of roadways in winter can be obtained from State and local transportation offices. Data should be collected on which roadways are regularly treated with salt and on the estimated application rate, such as tons of salt per lane mile.

The above listing provides an orderly basis for identifying the principal sources and causes of groundwater pollution within a monitoring area. An important footnote is that the listing stresses present-day sources and causes; however, historical sources and causes which are no longer present or active, such as former refuse dumps, brine disposal ponds, and feedlots, among others, may still be responsible for pollution today. This occurs because of the relatively long residence time of pollutants in most groundwater systems, which may be on the order of decades or centuries. It follows, therefore, that while identifying present sources and causes, an effort should also be made to find previous ones that may no longer be visible on the landscape but may be quite evident underground. Examination of old land use or zoning maps and early aerial photographs should prove helpful for this purpose. Furthermore, conversations with long-time residents who are knowledgeable of local activities may reveal information about pollution sources in previous times.

Step 3 — Identify Potential Pollutants

Having identified the pollution sources and the methods of disposal, the next step is to identify potential pollutants for each source. Major determinations in a water analysis are classified into physical, inorganic chemical, organic chemical, bacteriological, and radiological (Table 2). Table 3 summarizes the major sources of groundwater pollution and the types of pollutant generally present. The trace element portion of the inorganic chemicals has been separated into another category for discussion purposes.

TABLE 2. CLASSIFICATION OF MAJOR POTENTIAL POLLUTANTS IN GROUNDWATER

Physical
- Temperature
- Density
- Odor
- Turbidity

Inorganic Chemical
- Major Constituents
- Other Constituents
- Trace Elements
- Gases

Bacteriological
- Coliform Group
- Pathogenic Microorganisms
- Enteric Viruses

Organic Chemical
- Carbon
- Chlorophylls
- Extractable Organic Matter
- Methylene Blue Active Substances
- Nitrogen
- Chemical Oxygen Demand
- Phenolic Material
- Pesticides (Insecticides and Herbicides)

Radiological
- Gross Alpha Activity
- Gross Beta Activity
- Strontium
- Radium
- Tritium

TABLE 3. MAJOR SOURCES OF GROUNDWATER POLLUTION AND TYPES OF POLLUTANTS

SOURCE	TYPE OF POLLUTANT					
	Physical	Inorganic Chemical	Trace Elements	Organic Chemical	Bacteriological	Radiological
Municipal						
Sewer Leakage	Minor	Primary	Secondary	Primary	Primary	Minor
Sewage Effluent	Minor	Primary	Secondary	Primary	Primary	Minor
Sewage Sludge	Minor	Primary	Primary	Primary	Primary	Minor
Urban Runoff	Minor	Secondary	Variable	Primary	Minor	Minor
Solid Wastes	Minor	Primary	Primary	Primary	Secondary	Minor
Lawn Fertilizers	Minor	Primary	Minor	Minor	Minor	Minor
Agricultural						
Evapotranspiration and Leaching	Minor	Primary	Minor	Minor	Minor	Minor
Fertilizers	Minor	Primary	Secondary	Secondary	Minor	Minor
Soil Amendments	Minor	Primary	Minor	Minor	Minor	Minor
Pesticides	Minor	Minor	Minor	Primary	Minor	Minor
Animal Wastes (Feedlots and Dairies)	Minor	Primary	Minor	Secondary	Primary	Minor
Stockpiles	Minor	Primary	Minor	Variable	Variable	Minor
Industrial						
Cooling Water	Primary	Minor	Primary	Minor	Minor	Minor
Process Waters	Variable	Primary	Primary	Variable	Minor	Variable
Storm Runoff	Minor	Secondary	Variable	Primary	Minor	Minor
Boiler Blowdown	Primary	Secondary	Primary	Minor	Minor	Minor
Stockpiles	Minor	Primary	Variable	Variable	Minor	Variable
Water Treatment Plant Effluent	Minor	Primary	Secondary	Minor	Minor	Minor
Hydrocarbons	Secondary	Secondary	Secondary	Primary	Minor	Minor
Tank and Pipeline Leakage	Variable	Variable	Variable	Variable	Minor	Variable
Oilfield Wastes						
Brines	Primary	Primary	Primary	Minor	Minor	Minor
Hydrocarbons	Secondary	Secondary	Secondary	Primary	Minor	Minor
Mining Wastes	Minor	Primary	Primary	Variable	Minor	Variable
Miscellaneous						
Polluted Precipitation and Surface Water	Variable	Variable	Variable	Variable	Variable	Variable
Septic Tanks and Cesspools	Minor	Primary	Minor	Secondary	Primary	Minor
Highway Deicing	Minor	Primary	Minor	Secondary	Minor	Minor
Seawater Intrusion	Primary	Primary	Primary	Minor	Minor	Minor

Physical parameters, such as temperature and density, are of most concern in industrial and oilfield wastes. Inorganic chemicals are generally of primary concern in virtually all wastes. Trace elements are of concern in most categories of sources other than agricultural. Organic chemicals appear to be of concern in wastes from many types of sources. Bacteriological parameters are of primary concern in municipal sources, animal wastes, and in septic tank effluent or cesspool wastes. Radiological parameters are generally only of concern in some industrial and mining wastes. Major attenuation mechanisms can operate on many physical, organic chemical, bacteriological, and radiological constituents in passage through the topsoil and adequate thicknesses of the vadose zone. However, in the case of inorganic chemicals, these attenuation mechanisms are less effective. The attenuation mechanisms are described in more detail in the following steps; however, they have been considered in identifying potential groundwater pollutants.

Table 4 represents the inorganic chemical pollutants and gases common in groundwater or wastes. Pollutants are grouped on the basis of major

TABLE 4. INORGANIC CHEMICAL POLLUTANTS

Major
- Calcium
- Magnesium
- Sodium
- Potassium
- Carbonate
- Bicarbonate
- Sulfate
- Chloride
- Nitrate
- Total Dissolved Solids
- pH
- Electrical Conductivity
- Oxidation Potential

Other Trace
- Vanadium
- Molybdenum
- Bromide
- Iodide
- Nickel
- Aluminum
- Cobalt
- Lithium
- Sulfide
- Beryllium

Others
- Silica
- Boron
- Fluoride
- Nitrogen Forms
- Phosphorus Forms
- Hardness

Gases
- Methane
- Hydrogen Sulfide
- Carbon Dioxide
- Dissolved Oxygen
- Residual Chlorine

Drinking Water Trace
- Iron
- Manganese
- Arsenic
- Barium
- Cadmium
- Hexavalent Chromium
- Copper
- Cyanide
- Lead
- Selenium
- Silver
- Zinc
- Mercury

constituents commonly found in groundwater, additional constituents of interest in water use, trace elements of interest for drinking water quality, and additional trace elements common in some wastes.

The reports by Todd and McNulty (1974) and Meyer (1973) contain information regarding case histories of groundwater pollution. Data on the common specific pollutants in the major pollution sources are discussed in the following paragraphs.

MUNICIPAL. Five major municipal sources of pollutants can occur.

Sewage Effluent. For most secondary treated sewage effluent, the common specific pollutants are similar to those found in raw sewage. Thus, this discussion pertains to leaking sewers also. The inorganic composition of sewage effluent usually reflects the inorganic composition of the water supply. Little or none of the inorganic chemicals is removed during secondary treatment. Many heavy metals such as zinc, copper, iron, manganese, chromium, cadmium, lead, mercury, cobalt, and arsenic may enter sewage as a discharge from industry. However, many of the trace metals are removed with the sewage sludge. About 50 milligrams per liter (mg/l) of organic matter is usually present in secondary sewage effluent. More than one-half of the effluent organics is generally soluble. Hunter and Kotalik (1973) and the American Chemical Society (1969) presented data on constituents in sewage effluent. The effects of sewage effluent disposal on groundwater were discussed by Ellis (1973), Hughes et al. (1974), Schmidt (1973), Bogan (1961), and Bouwer et al. (1972).

Sewage Sludge. Peterson et al. (1973) discussed the constituents in sewage sludge. Most constituents considered under "sewage effluent" would be applicable, except there is more emphasis on trace elements, as those found in raw sewage are commonly concentrated in the sewage sludge. There have been few reported groundwater quality investigations beneath sludge drying beds; however, there is little doubt that this is a major point source of groundwater pollution.

Storm Runoff. The pollutants in storm runoff have been more widely recognized subsequent to the large-scale separation of this waste from sewage. Of concern to groundwater pollution is the presence of nitrogen and phosphorus, trace elements, and organic chemicals. High contents of lead and zinc have commonly been found in storm runoff. Gasoline, oil, grease, and pesticides are also common. (Sartor and Boyd, 1972).

Solid Wastes. Leachate analyses are highly variable; however, the major inorganic chemical constituents are usually present. Trace elements include iron, manganese, barium, chromium, lead, selenium, zinc, and possibly others. Organic chemicals are abundant in leachate. Hughes et al. (1971), Schneider (1970), California Department of Water Resources (1969), Weaver (1964), and Salvato et al. (1971) discussed constituents in solid wastes. There are a large number of evaluations concerning the effects of leachates on groundwater quality. Zanoni (1971), Apgar and Langmuir (1971), Kimmel and Braids (1974), Zenone et al. (1975), Weist and Pettijohn (1975), Coe (1970), Seitz (1972), and Andersen (1972) have reported on these evaluations.

Lawn Fertilizers. Primary concerns in lawn fertilizers are nitrogen, phosphorus, and potassium. Fertilizers are discussed more extensively under the section on Agricultural Sources.

AGRICULTURAL. Water percolating past the root zone in irrigated areas commonly is degraded compared to the applied water. This degradation is due to evapotranspiration, leaching of salts from the soil, and additives applied in the irrigation water, such as fertilizers, soil amendments, and pesticides.

Evapotranspiration and Leaching. Of major concern here are the major inorganic chemical constituents. In general the most mobile or soluble constituents will be concentrated the most by evapotranspiration. Of the major chemical constituents, sodium, chloride, nitrate, and boron are the most mobile in usual soil-groundwater systems. Law et al. (1970), Skogerboe and Law (1971), Flack and Howe (1974), and Fuhriman and Barton (1971) discussed return flow from agricultural lands. Mineral dissolution can occur in all areas. Salts in the topsoil and vadose zone in arid areas can also be dissolved by waters percolating from irrigation. Of most concern are sodium, calcium, chloride, bicarbonate, boron, and total dissolved solids. Doneen (1967) and the University of California at Davis (1968) discussed these phenomena for newly-developed lands in California.

Fertilizers. The primary fertilizers are nitrogen, phosphorus, and potassium. Significant amounts of other major chemical constituents can be added in compound form with the fertilizer, such as chloride in potassium chloride. Secondary fertilizers are calcium, magnesium, sulfur, boron, manganese, copper, zinc, molybdenum, chloride, cobalt, vanadium, and sodium. The major concerns in most groundwater systems are nitrate and the accompanying increase in salinity related to the application of nitrogen. Ammonia also has the ability to replace many other cations on the exchange complex of the soil thus allowing them to be leached into the groundwater. The literature is voluminous, and often contradictory, on the effects of fertilizers on groundwater quality. Mink (1962), Moore (1970), Willrich and Smith (1970a), Tisdale and Nelson (1966), Fitzsimmons et al. (1972), and Shaw (1968) have discussed fertilizers and groundwater pollution.

Soil Amendments. The most common soil amendments of importance to groundwater pollution are gypsum, lime, and manure. Manure, in part, falls under the fertilizer category. Gypsum contains calcium and sulfide, and lime commonly contains calcium or calcium and magnesium carbonate. Sulfur may be applied to calcic solid in the elemental form. The pH and bicarbonate are important parameters, as lime is frequently applied to change the soil pH. When gypsum is applied, it frequently results in the leaching of sodium held in the soil, along with sulfate. Buckman and Brady (1969) discussed soil amendments and their use in agriculture.

Pesticides and Herbicides. Pesticides, herbicides, fungicides, and other chemicals are used for nuisance organism control. Drinking water standards are proposed for the common chlorinated hydrocarbons and for total organophosphorus and carbamate compounds. Thus, for monitoring groundwater pollution, DDT, 2,4-D, lindane, and herbicides are major concerns. Willrich and Smith (1970b), California Department of Water Resources (1968), Johnston et al. (1967), Scalf et al. (1968), Dregne et al. (1969), and Schneider et al. (1970), discussed pesticides and groundwater pollution.

Animal Wastes. Constituents of concern in animal wastes are somewhat similar to those found in human sewage, including many of the major inorganic chemical constituents, particularly nitrate, chloride, sulfate, and total dissolved solids. Organic matter and bacteriological constituents are also present. Willrich and Smith (1970c), Stewart et al. (1967, 1968), Loehr (1967), Concannon and Genetelli (1971), Gillham and Webber (1969), and Adriano et al. (1971) have discussed animal wastes and groundwater pollution.

INDUSTRIAL. Pollution from industry includes the following six types.

Cooling Water. Major degradation of cooling water results from temperature increases and possibly from some trace elements introduced as additives, such as rust inhibitors. If large amounts of evaporation occur brines may result, and concerns for overall salinity and the major inorganic chemical constituents would be increased.

Process Water. Industrial process water is highly variable; however, in general, trace elements will be of major concern. These could be introduced from raw materials and chemicals used in the process. Temperature and density could be important. The major inorganic chemical constituents would usually be of concern, as well as overall salinity. Organic chemicals would be common constituents, such as hydrocarbons, reagents added for processing, etc. Radioactive components are important in the disposal of nuclear plant wastes and certain other operations. Radium, strontium, and alpha and beta activity are major criteria for drinking water.

Storm Runoff. The quality of storm runoff is highly influenced by housekeeping procedures and drainage systems. If significant amounts of solids and liquids are spilled, blown by the wind, and left to accumulate on the topsoil or impermeable surfaces, they can be subsequently mobilized by storm runoff. The major concerns are organic chemicals, such as hydrocarbons, and possibly trace elements. Major inorganic chemicals are also important.

Boiler Blowdown. Major concerns with boiler blowdown water are temperature and several of the major inorganic chemicals, namely, silica, calcium, magnesium, bicarbonate, and selected trace elements.

Stockpiles. Stockpiles for storage of raw materials, products, byproducts, and wastes at industrial sites would be highly variable, somewhat similar to process water. However, physical parameters would generally be of less importance.

Water Treatment Plant Effluent. Some of the major inorganic chemicals would be of concern, particularly sodium, chloride, calcium, sulfate, bicarbonate, and nitrate, and total dissolved solids. In some cases, selected trace elements may be of concern.

Studies of industrial waste pollution of groundwater are numerous. Examples are Tucker (1971), Smith (1971), Williams and Wilder (1971), Matis (1971), Sweet and Fetrow (1975), Walker (1961), Deutsch (1961), Walton (1961), and Hanby et al. (1973).

OILFIELD WASTES. Brines and hydrocarbons are present in oilfield wastes.

Brines. Density and possibly temperature could be important for oilfield brines. The major inorganic chemical constituents are of concern, particularly sodium, chloride, calcium, sulfate, bicarbonate, and total dissolved solids. Boron, ammonium, fluoride, bromide, and iodide are also common in brines. Many trace elements are commonly present such as lead, iron, strontium, zinc, manganese, nickel, and aluminum.

Hydrocarbons. Materials such as oil can pollute groundwater, and thus hydrocarbons are of major concern.

References by Mattox (1970) and White et al. (1963) detail the composition of saline waters. Many references have documented groundwater pollution from disposal of oilfield wastes, such as Fryberger (1975), Pettyjohn (1972), Bain (1970), Krieger and Hendrickson (1960), Knowles (1965), and McMillion (1965).

MINING WASTES. Waste production from mining activities has been discussed in detail by Williams (1975). In general the major inorganic chemical constituents will be important and often trace elements will be of primary concern. Nitrogen forms may be used in explosives and could appear in the groundwater. Trace elements will depend on constituents of ore processed and reagents added. Organic chemicals may be added as reagents and radiological constituents may be present in the ore.

MISCELLANEOUS. Miscellaneous sources of pollution are the following.

Septic Tanks and Cesspools. The constituents of importance are generally similar to those in sewage effluent, except trace elements will usually be absent. Also the chances for nitrification in the topsoil or vadose zone are generally better in the case of septic tanks. Polta (1969), Waltz (1971), Schmidt (1972), Quan et al. (1974), and Pitt (1974) have discussed the groundwater pollution due to individual sewage disposal systems.

Highway Deicing. Of primary concern in highway deicing are sodium, chloride, and calcium. Some organic chemicals are periodically used.

Saline Water Intrusion. The same constituents are of interest as for brines under Oilfield Wastes.

Step 4 — Define Groundwater Usage

To evaluate the impact of pollution or potential pollution of groundwater, the usage of the resource becomes a key item. Thus, it is important to define both the quantities of groundwater being extracted or projected to be extracted, and the locations of major pumping centers within a monitoring area. Pumpage data on a gross basis are usually available from the U. S. Geological Survey, State water agencies, and some local water agencies. Often it will be necessary to refine the data in order to make them useful in developing an effective monitoring program.

Pumpage will usually vary on a weekly and on a monthly basis; however, in many cases mean annual extractions will be sufficient to evaluate groundwater flows and pollutant movement for monitoring purposes. These data will serve as inputs to the hydrogeologic analysis in a subsequent step.

Determination of groundwater pumpage depends on the type of use. The basic categories of use — municipal, industrial, agricultural, and rural — are described below in terms of how their pumpage quantities can be defined.

MUNICIPAL USE. Groundwater pumpage for an urban area is often available from records of water purveyors. Furthermore, locations and yields of individual wells and well fields are usually known.

INDUSTRIAL USE. Many industries purchase water from municipal sources; consequently, under these circumstances groundwater use is incorporated in the municipal category. On the other hand, some industries use self-supplied water, and a portion of these draw upon groundwater through wells. On a national basis the following types of industries are the heaviest users of groundwater:

Rank in Terms of Total Groundwater Use	Type of Industry
1	Oil Refining
2	Paper Manufacturing
3	Metal Working
4	Chemical Manufacturing
5	Building, Air Conditioning and Refrigerating
6	Distilling
7	Ice Manufacturing and Cold Storage
8	Food Processing
9	Rubber Manufacturing
10	Meat Packing
11	Brewing
12	Railroad Yards
13	Gas and Electricity
14	Dairying
15	Electric Equipment Manufacturing

If no local summary of industrial use of self-supplied groundwater is available from appropriate public agencies, pertinent industries will have to be identified. Industrial areas can be located from aerial photographs or zoning maps; industries which do not receive municipal water can then be contacted to obtain their annual groundwater pumpage data. Often these are not directly available and must be estimated from the type of industry, number of workers, units of production, or other factors.

AGRICULTURAL USE. In the Western United States groundwater is used mostly in irrigated agriculture; however, data on such usage are also generally difficult to obtain. Accurate records of pumpage are rarely kept by farmers, and, in fact, most irrigation wells are not equipped with flow meters. Pumpage estimates can be made by either of two methods. One is to determine cropping patterns of areas irrigated by wells, using aerial photographs and crop surveys. By knowing the consumptive use of the crops and representative irrigation efficiencies (from local farm advisors) and mean annual growing season rainfall (from U.S. National Weather Service records), the total applied water for irrigation purposes can be computed. In areas where both surface water and groundwater are used, the portion of applied water supplied by groundwater can usually be determined from irrigation district records. A second approach is to obtain records of power consumption for representative pumps and of pump discharges per unit of power use from electric utility companies. These data enable the quantities of water pumped to be calculated. Where such data are available for only a fraction of the irrigated area, extrapolation to the gross area can be made; however, results can be subject to error if significant differences in pumping levels exist.

RURAL USE. Data will rarely be available on pumpage from individual domestic water supply wells in rural areas. Estimates of pumpage can be made, however, by multiplying rural population figures by typical per capita water use. In general, these pumpage rates are so scattered over agricultural areas that they do not influence the groundwater flow. However, the existence of the rural use should be recognized, particularly in the event of a localized pollution problem.

In summary, the total of the four above groundwater uses provides the usage data for a monitoring area. Locations of major pumping centers, such as well fields of municipalities and large industries, should be identified. Average pumpage rates over uniform subareas, such as irrigated lands, should be defined from irrigation well pumping rates and well densities. Great precision in determining groundwater pumpage is not as important as a comprehensive coverage of all significant pumpage within an area.

Step 5 — Define Hydrogeologic Situation

To understand where and how groundwater pollution occurs and moves within a monitoring area, the hydrogeologic framework must be understood. This information will aid in the design of an effective as well as an efficient groundwater quality monitoring system.

Because some subsurface data are available in most areas of groundwater development, initial hydrogeologic work will consist of gathering, organizing, and analyzing existing information. On other occasions, geologic or hydrologic investigations requiring field work will be necessary. Specific materials needed for the monitoring program, as well as how they are obtained, include:

- Aquifer locations, depths, and areal extents — from geologic data
- Transmissivities of aquifers — from well pumping tests and geologic data
- Map of groundwater levels — from observations of well levels
- Map of depths to groundwater — from water level and topographic data
- Areas and magnitudes of natural groundwater recharge — from precipitation, evapotranspiration, soils, land use, and water level data
- Areas and magnitudes of artificial groundwater recharge — from irrigation and recharge data
- Areas and magnitudes of natural groundwater discharge — from streamflow and water level data

- Directions and velocities of groundwater flows — from water level and transmissivity data.

Information sources for preparation of the above items should normally include State geologic and water agencies, local water agencies, the U. S. Geological Survey, and the U. S. National Weather Service.

In preparing the above materials it should be kept in mind that these serve as tools for monitoring; consequently, the hydrogeologic effort should not become an obstacle to the completion of the monitoring program. All hydrogeologic data are incomplete in a relative sense. What is needed is an overall picture of the hydrogeologic situation in the monitoring area. Initially, refinement is less important than comprehensive coverage, no matter how preliminary or approximate. Categories indicating ranges rather than specific values, such as for transmissivity or dissolved solids, are often sufficient. Also, it should be recognized that with time and with increasing amounts of groundwater data, knowledge of the hydrogeologic situation will gradually improve.

EXAMPLE 1 — POLLUTION PLUME GEOMETRY. Figure 2 shows examples of the configurations of pollution plumes resulting from a pollution source, such as a landfill, located near a river. In Figure 2(A) the angle between the groundwater flow direction and the river is relatively large. This limits the extent of the plume; furthermore, where the source is located close to the river, the plume is smaller. In Figure 2(B) the angle between the groundwater flow direction and the river is relatively small; this creates elongated plumes, particularly where the source is some distance from the stream.

EXAMPLE 2 — GROUNDWATER FLOW SYSTEM. Figure 3 depicts schematically a groundwater flow system under idealized homogeneous aquifer conditions. Groundwater travels along flow paths which extend from areas of groundwater recharge to areas of groundwater discharge. Horizontal and vertical gradients are indicated by equipotential lines; potential, or total head, is simply the elevation to which water will rise in a cased well from a point source below the water table. Groundwater moves in the direction of decreasing total head. In recharge and discharge areas, movement may have an appreciable vertical component; between these end areas, flow is predominantly horizontal. Any pollution will travel along the flow line where it occurs.

EXAMPLE 3 — COMPLEX PLUME GEOMETRIES. Figure 4 presents an idealized vertical aquifer cross-section, somewhat similar to Figure 3, together with the pollution plumes for various locations of pollution sources. Note that Sources A-1 and A-2 create short plumes because they are close to streams, while B and C are longer because they are more distant. Source F, located in a discharge area, has no effect on groundwater quality.

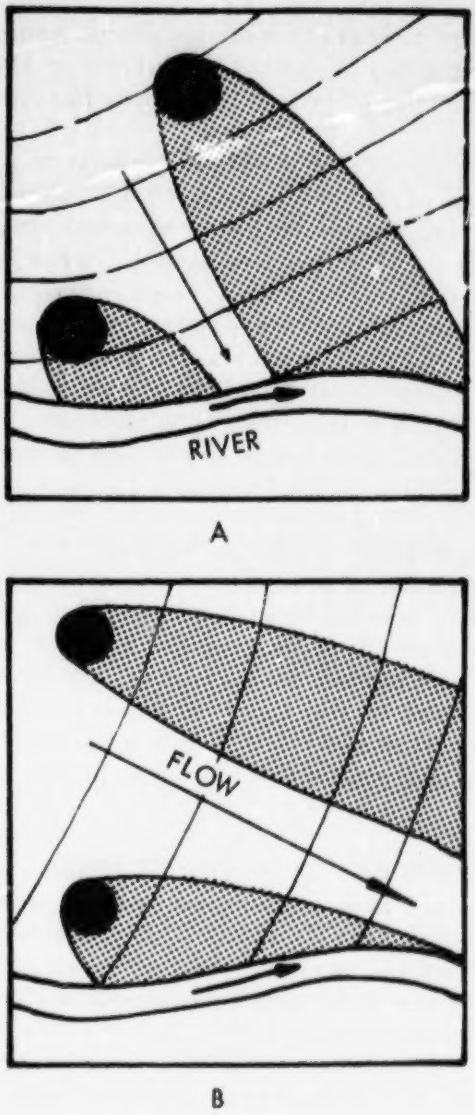


Figure 2. Relation of groundwater pollution plume size and orientation for a pollution source near a river with different groundwater flow directions (Palmquist and Sendlein, 1975).

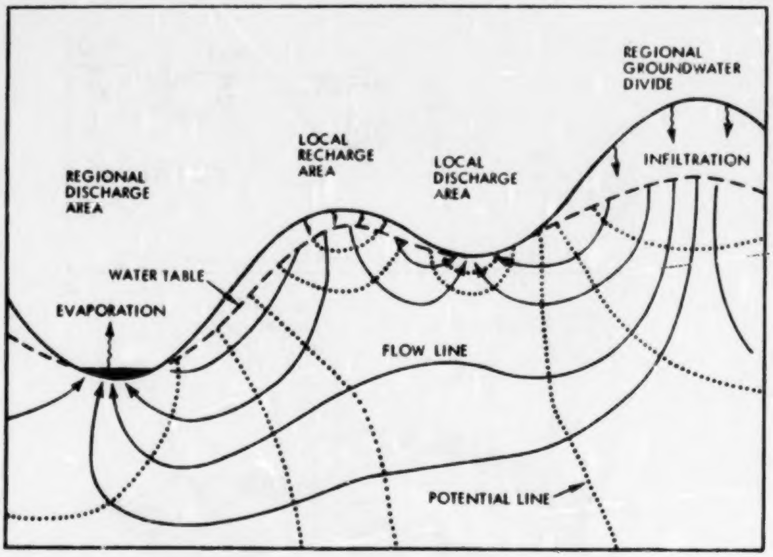


Figure 3. Groundwater flow system under idealized homogeneous aquifer conditions (modified after Born and Stephenson, 1969).

Sources D and E-2 cause two plumes in different directions, while E-1 is responsible for three distinct plumes. Clearly, recognition of the hydrogeological conditions controlling the number, shape, and locations of pollution plumes is essential in selecting groundwater monitoring sites.

EXAMPLE 4 – POLLUTION FROM A PERCOLATION POND. Figure 5 illustrates how hydrogeologic conditions can influence the movement of pollution from a percolation pond. Here the aquifer is recharged by a lake on the north side, while on the southwest a river both recharges and receives discharge from the aquifer. Near the center of the aquifer a well field creates a radially converging flow pattern, and south of it is located a recharge pond which is maintained at a constant water level. Flow lines of groundwater for steady-state conditions are shown on Figure 5. In addition, it is assumed that at a certain time, pollution is introduced into the pond. By means of an electronic analog model, the advancing pollution front can be calculated. Positions of the front for 40 and 80 days after the beginning of pollution are shown in Figure 5. Note that between these two time intervals pollution has reached both the well field and the river. The dashed lines define the ultimate limits of pollution from the percolation pond.

EXAMPLE 5 – EFFECT OF PUMPING ON GROUNDWATER FLOW. Figure 6 provides dramatic evidence of how heavy pumping in an urban area can influence groundwater flow directions. Solid lines are water table contours; these show that the water table is more than 70 feet below sea level

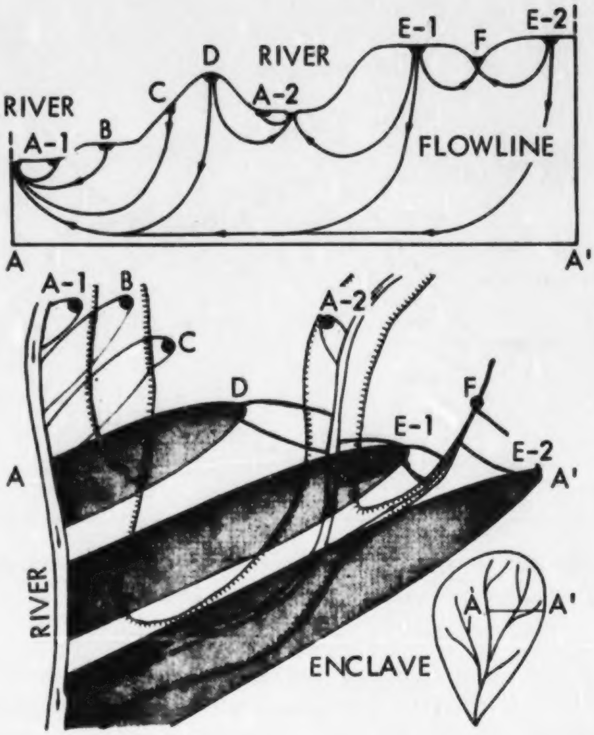


Figure 4. Idealized pollution plume configuration for various locations of surface pollution sources (modified after Palmquist and Sendlein, 1975).

in the center of Stockton, California. It can be seen that any pollutants in the groundwater are transported toward the city from a large area. If such a cone of depression results from pumping of water supply wells, the concentrating effect of the wells moves all pollution into them, which is clearly undesirable.

EXAMPLE 6 – DENSITY EFFECT ON POLLUTION DISTRIBUTION. Figure 7 shows the distribution of saline water below a brine disposal pit in an oil field in southwestern Arkansas. Because the brine is denser than native groundwater, it has traveled to the bottom of the sandy confined aquifer and thereafter has spread laterally. The primary extension of pollution is southward due to the natural groundwater gradient in this direction. If the pollutant had possessed a density more nearly that of the native groundwater, it would be expected to drift horizontally near the top of the aquifer. Thus, the physical character of a pollutant can have a significant effect on how it moves within an aquifer.

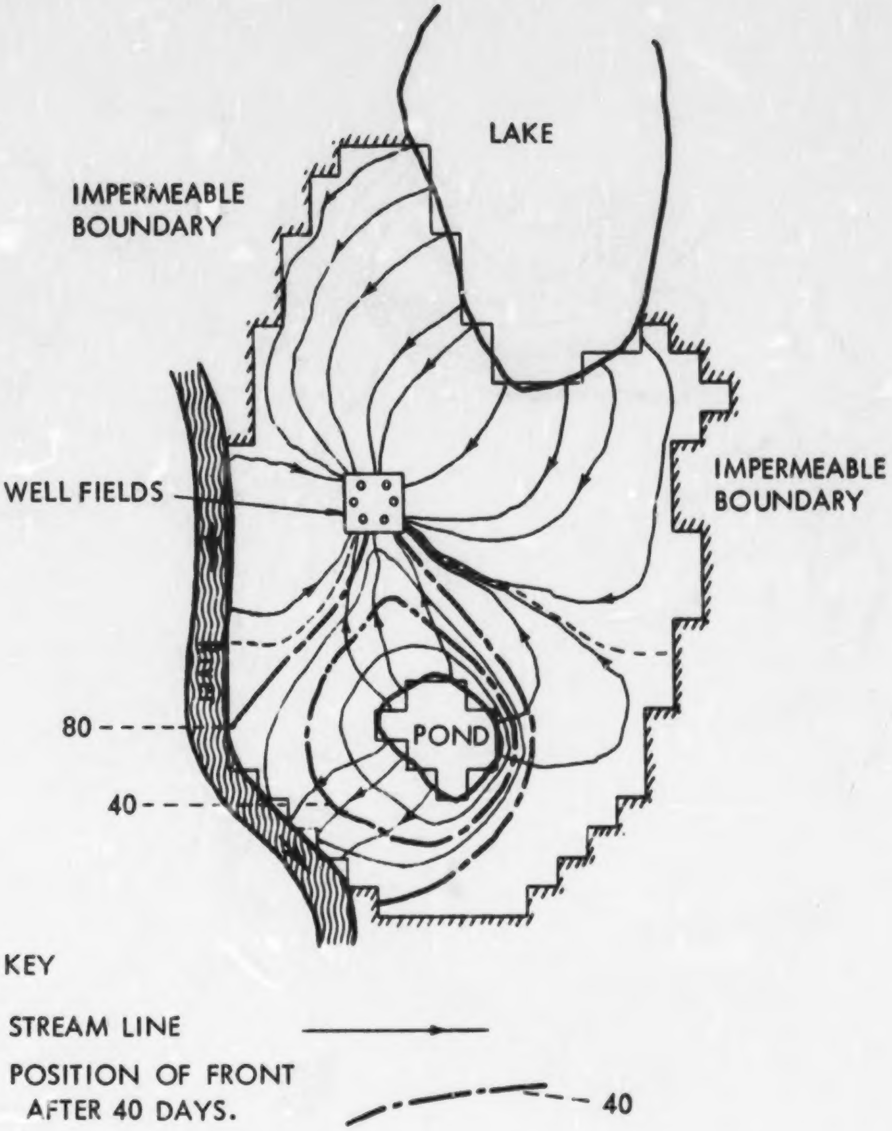

LAKE
IMPERMEABLE BOUNDARY
WELL FIELDS
IMPERMEABLE BOUNDARY
80
40
POND
KEY
STREAM LINE
POSITION OF FRONT AFTER 40 DAYS.
40

Figure 5. Flow lines for steady-state conditions in an aquifer and positions of a pollution front advancing from a percolation pond (Cole, 1975).

Step 6 — Study Existing Groundwater Quality

In order to define the groundwater quality problems within a monitoring area, an assessment needs to be made of the background quality situation. To do this, recent groundwater quality data need to be collected and reviewed. Attention should be focused first on the natural groundwater

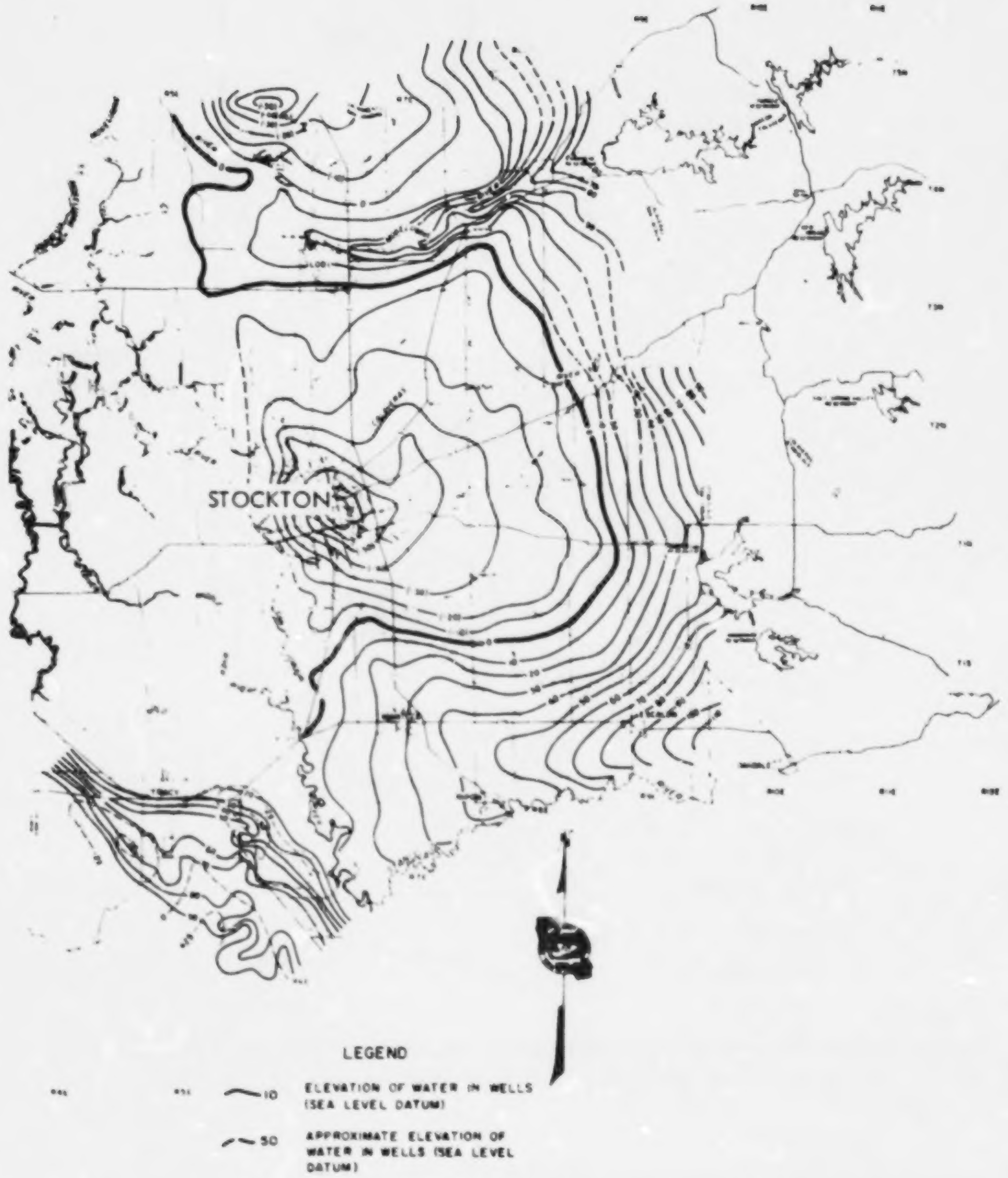

STOCKTON
LEGEND
10 ELEVATION OF WATER IN WELLS (SEA LEVEL DATUM)
50 APPROXIMATE ELEVATION OF WATER IN WELLS (SEA LEVEL DATUM)

Figure 6. Water table contours in the vicinity of Stockton, California, Fall 1964 (California Department of Water Resources, 1967).

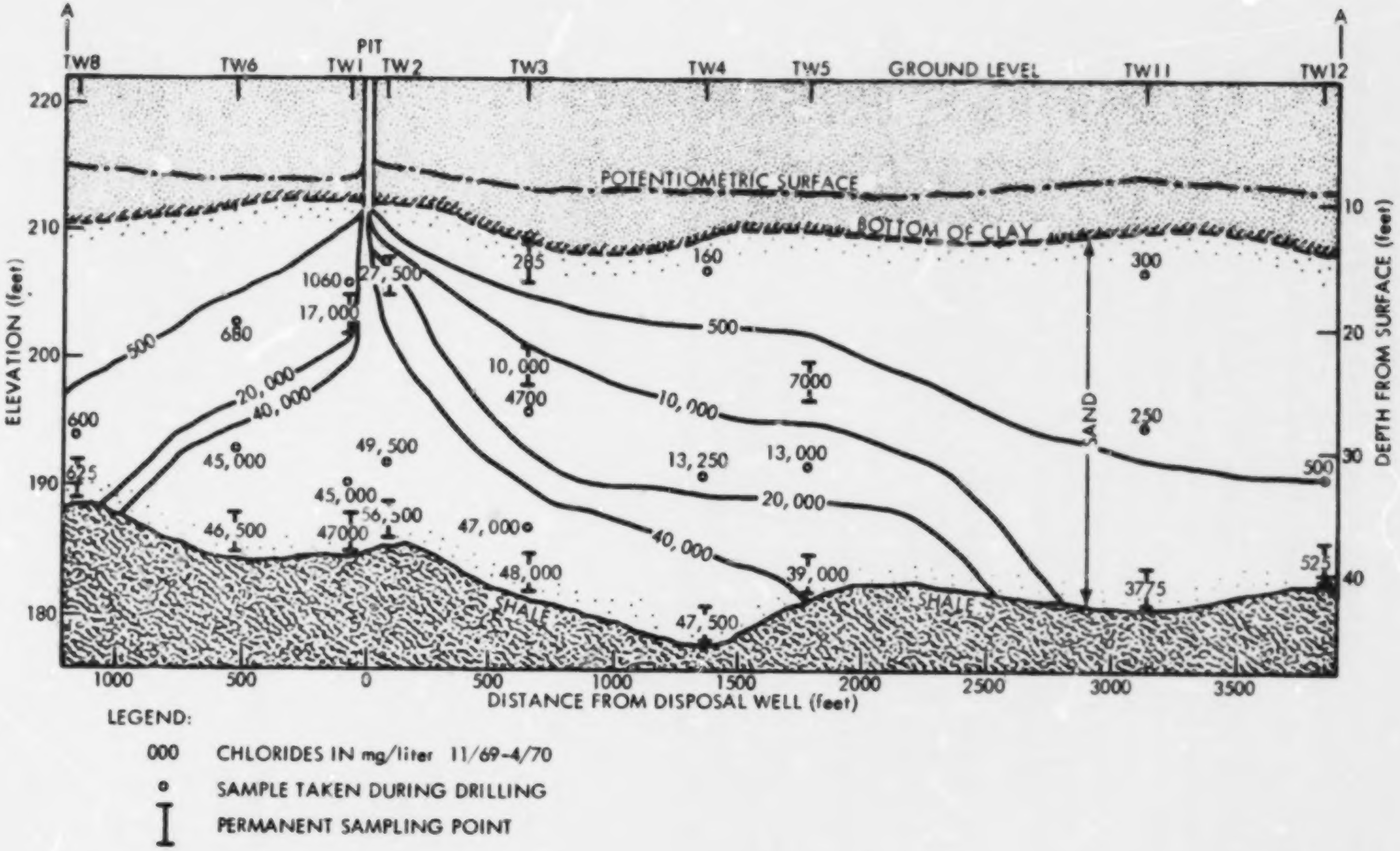

A
A
PIT
TW8
TW6
TW1
TW2
TW3
TW4
TW5
GROUND LEVEL
TW11
TW12
220
210
200
190
180
ELEVATION (feet)
10
20
30
40
DEPTH FROM SURFACE (feet)
POTENTIOMETRIC SURFACE
BOTTOM OF CLAY
SAND
SHALE
SHALE
500
20,000
40,000
500
10,000
20,000
40,000
600
625
680
45,000
46,500
1060
17,000
27,500
49,500
45,000
47000
56,500
285
10,000
4700
47,000
48,000
160
13,250
47,500
7000
13,000
39,000
300
250
3775
500
525
1000
500
0
500
1000
1500
2000
2500
3000
3500
DISTANCE FROM DISPOSAL WELL (feet)
LEGEND:
000 CHLORIDES IN mg/liter 11/69-4/70
○ SAMPLE TAKEN DURING DRILLING
I PERMANENT SAMPLING POINT

Figure 7. Distribution of saline water in a confined aquifer resulting from an oilfield brine disposal pit in southwestern Arkansas (modified after Fryberger, 1975).

quality. A map of indicators of pollution in groundwater, taking into account variations as a function of depth, should be prepared from available well water analyses. This map will typically show a limited range of values within an extensive aquifer. However, if considerable variability or isolated anomalies are evident, these may be indicative of the presence of pollution.

To verify possibilities of pollution, regions or localities displaying unusual quality data must then be examined in conjunction with the inventory of pollution sources and methods of disposal (Step 2) and with hydrogeologic data (Step 5). Where these jointly suggest the physical feasibility of pollution, it is reasonable to assume that pollution exists. Once pollution is tentatively identified, the specific pollutants involved, the areal extent, and the direction and rate of movement can be defined at least approximately.

It is often surprising how many quality data, after investigation, are actually available. A certain amount of ingenuity is required to locate fragmented data and to interpret them in terms of the subsurface situation. Judgment, however, must frequently be exercised so as to select meaningful data and to avoid those which are erroneous.

In addition to collecting current data, past groundwater quality records should be reviewed wherever possible. Historical quality records are helpful in establishing the quality of native groundwater, in evaluating quality trends with time and in relating changes in groundwater quality to sources and causes.

Information sources for groundwater quality data should normally include State geologic and water agencies, the U.S. Geological Survey, local water and regulatory agencies, and industries with self-supplied groundwater.

It should be recognized that significant portions of a monitoring area may entirely lack groundwater quality data, so that no direct indications of pollution can be obtained. However, sources and causes as well as hydrogeologic evidence may suggest locations of potential pollution. Verification can only come with the implementation of the monitoring program.

Step 7 — Evaluate Infiltration Potential of Wastes at the Land Surface

Following the development of an understanding of the hydrogeologic framework, a key step in the methodology will be to determine the volume of polluted water which will pass through the vadose zone into the zone of saturation. This volume will vary depending on the method of waste disposal used and the infiltration characteristics of the soil. The monitoring methods applicable to the above determination are discussed in detail in Section III of a companion report (Everett et al., 1976).

Considering the common methods of waste disposal presented previously in Step 2, Table 1, the total volume of polluted water associated with surface spreading, irrigation, or disposal into dry stream beds, will move directly into the topsoil or stream bed. The volume of polluted water associated with percolation ponds, seepage pits, trenches, or landfills will bypass the topsoil and enter the underlying portion of the vadose zone or saturated zone depending on the depth to the water table.

Disposal wells used to dispose of storm water and domestic sewage frequently are terminated in the vadose zone. The volume of polluted water reaching the zone of saturation will be equal to the volume discharged into the well, minus that portion retained by the soil. A properly designed injection well for disposal of industrial wastes or brines will completely bypass the vadose zone and all freshwater aquifers. Monitoring procedures for injection wells are discussed at length by Warner (1975).

The water budget method can be used to calculate infiltration from surface spreading or irrigation. In the water budget approach, waste water discharge and precipitation are volumetrically summed as the input, and infiltration is computed as the difference between this input and evapotranspiration. Applied water volumes can be determined from records of waste water discharge/surface water deliveries, and groundwater pumpage. Precipitation volumes can usually be extrapolated from rainfall gaging stations in nearby areas. Monthly rainfall determinations are often suitable; however, in areas with highly variable precipitation, such as in Southwestern States, onsite measurements may be necessary.

Evapotranspiration from areas where surface spreading or irrigation is used can be determined by a number of methods (Cruff and Thompson, 1967; Blaney and Criddle, 1962; Lowry and Johnson, 1942; Penman, 1948; and Thornthwaite, 1948). These methods are generally based on different groupings of climatological parameters. For example, the Blaney-Criddle method depends primarily on temperature and percentage of daylight hours. In general the Penman and Thornthwaite methods are more applicable to humid areas, whereas the Blaney-Criddle method is more applicable to semiarid areas.

Different values of evapotranspiration and consumptive use are usually obtained for different crops and soil conditions. Thus, the cropping pattern must be known, and factors such as double-cropping considered. Sufficient field tests have been conducted in many areas so that evapotranspiration and consumptive use for major crops are well established. In some areas, data may have to be extrapolated from similar areas. Evapotranspiration rates will generally be needed on at least a monthly basis, and sometimes weekly.

In summing up the water budget components for surface spreading and irrigation, the infiltrating component is divided into two components. A portion of this component is diverted into soil moisture retention. This soil moisture component will be gradually depleted by transpiration during periods of zero recharge. When the field capacity requirements have been satisfied the remaining portion will percolate to the zone of saturation.

In many parts of the arid and semiarid West, significant volumes of waste waters are disposed of into normally dry stream channels. Disposal of mining wastes and sewage effluent in Arizona and oilfield wastes in California by this method is common. That portion which does not leave the area as runoff or evaporate infiltrates into the stream bed. Part of the percolate will be held in storage and the remainder will flow on to the zone of saturation. The portion held in storage will be quite small relative to that of a normal soil profile because of the high permeability associated with stream bed materials.

Stream flow records at different gaging stations along the particular reach under investigation, combined with records of precipitation, evaporation, estimates of soil moisture content, and stream flow diversions, can be used to calculate percolation to the water table. In some areas the U.S. Geological Survey, State geological or water agencies, or others may have already made estimates of infiltration.

The water budget method can also be used to calculate seepage from percolation ponds. In this context, "percolation pond" is used to signify any pond which permits significant movement of water into the underground. Waste discharge and precipitation are volumetrically summed as the input, and seepage is calculated as the difference between input and evaporation. Storage changes in the pond must also be taken into account. Evaporation from free-water surfaces can be determined from measurements using land pans or floating pans (Harbeck et al., 1958; Kohler et al., 1955; Follansbee, 1933; and Rohwer, 1933). Monthly values will often suffice; however, in some cases weekly or daily values are necessary.

Factors such as salinity of waste water can affect the evaporation rate. In general, with increasing salinity the vapor pressure of water decreases, resulting in a lower evaporation rate. In considering evaporation from free-water surfaces from ponds of different sizes, consideration should be given to edge effects. That is, evaporation rates depend on the characteristics of the surrounding land, for example, whether it is cultivated or undeveloped.

In some ponds such as mine tailings ponds, water may occur in several states — such as free water, moist tailings, and wet tailings. Where ponds are periodically dried to improve infiltration rates, evaporation from moist areas and wet areas must be considered separately from the free-water evaporation. Methods for determining such evaporation are not well developed. Field measurements using lysimeters can be used as an independent check on evaporation from soil surfaces. It may be sufficient to apply correction factors to the evaporation rate calculated from lysimeters for use in free-water surfaces.

Effluent from septic tanks and other wastes is commonly disposed of in seepage pits or trenches which extend only a few feet beneath the land surface. As such, these wastes usually are subject to the effects of evapotranspiration. Determination of evapotranspiration is difficult because of varying soil conditions, septic tank disposal practices, vegetation type and distribution, and other factors. Evapotranspiration is the sum of evaporation from bare soil surfaces and transpiration by vegetation growing in the area. Rooting depth would be a key factor in plant uptake of effluent from trenches. If the land surface is irrigated this must also be considered. Generally, if leach lines are placed at depths greater than about 5 feet in most soils in the absence of deep rooted plants, seepage is virtually the same as the waste discharge. If trenches are only a few feet beneath the land surface, then a water budget analysis may be made. This analysis would usually be done for groups of septic tanks, such as for a subdivision in an urban area. Precipitation is combined with waste discharge as the input, while evapotranspiration and runoff are losses. The residual seepage is subject to a soil moisture retention loss, depending on the depth to the water table from the bottom of the trench.

Landfills pose a threat to groundwater quality depending on the volume of leachate leaving the fill. This in turn is a function of the leachate control methods in use for a particular landfill, such as clay liners, collection and treatment, impermeable rubber or plastic barriers and caps. Many landfills have not been properly designed and as a consequence are almost certain to produce leachate.

The water budget method may be applied when estimating leachate production from landfills. Precipitation volumes must be obtained and the portion that infiltrates the landfill determined. This portion will first go into meeting the moisture storage requirements of the solid waste. For this reason the moisture content of the solid waste must be estimated. When the solid waste reaches field capacity leachate will result. Whether this leachate will reach the zone of saturation will depend on the leachate control method in use.

The leachate produced from a landfill can be estimated using the following relationship:

$$\text{Leachate} = P - R - ET - S$$

where

P = precipitation

R = runoff

ET = evapotranspiration

and

S = the field capacity of the solid waste minus its existing moisture content.

Step 8 — Evaluate Mobility of Pollutants from the Land Surface to Water Table

The topsoil and materials of the vadose zone may have a significant capacity to remove pollutants from downward-percolating waters. The extent of groundwater pollution due to waste percolation from the land surface depends strongly on the rate and volume of recharged water. In a semiarid or arid climate, pollutants may be retained above the water table in a nearly permanent fashion. On the other hand, in humid areas pollutants may be rapidly carried downward from the land surface to the water table. Generally, in a homogeneous porous media, percolating water will pass vertically through the vadose zone. However, in a heterogeneous, stratified material, such as most of the alluvial deposits of the western U.S., percolating water may become perched above layers of low permeability. In this situation, lateral movement for substantial distances can occur above the water table.

The capacity for attenuation of many potential pollutants is greatly limited by the amount and characteristics of the geologic materials present in the vadose zone. This is especially true for the sorption capacity of many organic chemicals, trace elements, and radionuclides. This limited capacity for removal of some pollutants is in sharp contrast to the almost unlimited ability of many unconsolidated materials to remove bacteriological pollutants. The existence of many documented case histories of groundwater pollution indicates that the vadose zone may often not provide complete protection. Problems can occur when the zone is bypassed during waste discharge or when attenuation capacity is exceeded due to high waste loadings.

Pollutant attenuation in the subsurface commonly occurs due to the following processes: dilution, filtration, sorption, buffering, precipitation, oxidation and reduction, volatilization, biological degradation and assimilation, and radioactive decay. Each of these processes must be evaluated with respect to specific pollutants.

DILUTION. Dilution above the water table can be substantial in humid areas and almost nonexistent in arid areas. Sources of water for dilution include precipitation, seepage from streams, lakes and canals, and artificial recharge. A water budget analysis can be used to evaluate the extent of dilution. Generally, the analysis is done in a similar manner to that discussed in the previous step concerning evaluation of infiltration potential. However, in this case, all items of recharge from the land surface are considered, such as canal seepage, percolation from streams and lakes, and artificial recharge in the area. The quality of water from each source of recharge must be determined. A comparison of the respective quantities of water and constituents concentrations in a waste discharge at the land surface can indicate the extent of subsequent dilution of pollutants.

An example is presented in the following discussion. Assume an agricultural area in the West where irrigation is practiced in the dry summer months and rainfall occurs in the wet winter months. Return flow over the area averages 18 inches per year and the salinity of this water is 300 parts per million (ppm). Rainfall is 12 inches per year and its salinity is 10 ppm. Consideration of the water budget analysis at the land surface indicates that 9 of the 12 inches of rainfall percolates to the water table. The subsequent dilution can be calculated by the equation:

$$AV_A + BV_B = C$$

where V_A and V_B are the respective percentages of water from return flow and precipitation. A, B, and C are the respective salinities of the return flow, precipitation, and the mixture of the two. In this example:

$$C = 300(18/27) + 10(9/27)$$

$$C = 200 + 3 = 203 \text{ ppm}$$

This dilution reduces the pollutant concentration by about one-third of the original value. This simple concept can be expanded to encompass dilution and a number of sources of pollution.

FILTRATION. Filtration removes virtually all of the suspended materials that would be of more concern in surface water pollution. However, this process is generally not effective for most of the inorganic chemical species. Exceptions include iron and manganese, which may be present in aerated waters as hydroxides in particulate matter. Similarly, as precipitates form due to chemical reactions, they may be effectively filtered out as water moves through porous media. For wastes with high iron or manganese contents, laboratory tests can be performed on soils or geologic materials of the vadose zone. However, other attenuation factors affecting the pollutants would have to be evaluated.

SORPTION. Sorption is probably one of the most effective processes for attenuating groundwater pollution. Clays, metallic oxides and hydroxides, and organic matter can all be suitable materials for sorption of various pollutants. With the exception of chloride, and to a lesser extent nitrate and sulfate, most pollutants can be sorbed and removed to some extent under favorable conditions. Under other circumstances, however, the pollutants can move freely through the porous media. The pH and oxidation potential often govern the extent of sorption for specific constituents. The sorption process depends on the type of pollutant and the physical and chemical properties of both solution and the containing materials.

When a pollutant in ionic form is sorbed, some other change must occur to compensate for loss of the ion from solution. In ion-exchange processes, a different ion is released by the solid to the water. However, this release is not required if the pollutants are sorbed or electrically neutral, such as most organics and neutral complexes of various metals.

The sorptive capacity can be estimated based on the density, clay content, and cation exchange capacity of the soil and geologic materials above the water table. Values for these parameters can be calculated from available data in soils and groundwater reports on the area of interest. In exceptional cases, these parameters can be determined from detailed onsite measurements. For calculation purposes, the thickness of the vadose zone is known or determined from water level data. For simplicity, the vertical path of polluted water from the land surface beneath the waste disposal area to the water table can be assumed to be the distance traveled.

As an example, assume the average density of materials in the vadose zone is 1.6 grams per cubic centimeter, the clay content is 20 percent by weight, and the clay has a cation exchange capacity of 70 milliequivalents per 100 grams. Each gram of clay will have the ability to remove 0.70 milliequivalents of the pollutant of interest. For example, for potassium (equivalent weight of 39), each gram of clay will have the ability to remove 27.3 (0.70x39) milligrams of potassium from the percolated waste water. Each gram of solid material will have the ability to remove 5.5 (0.20x27.3) milligrams of potassium from the percolated waste water. With a density of soil of 1.6 grams per cubic centimeter, one acre-foot (1.2335×10^9 cubic centimeters) of soil would contain 1.97×10^9 grams of solid material. This soil could sorb 23,900 pounds of potassium. For a vadose zone 50 feet thick, one acre of the vadose zone could sorb over one million pounds of potassium.

To determine the actual extent of adsorption, laboratory tests can be performed utilizing soils and geologic materials typical of the waste disposal site. The actual waste discharge can be used or a similar synthetic solution prepared. Hajek (1969) summarizes laboratory procedures for such tests.

It should be noted that percolating fluids may subsequently remobilize species that have been sorbed. The sorptive capacity of soils and geologic materials is finite for most inorganic substances which cannot be biodegraded. However, for substances which are biodegradable, such as many bacteriological constituents and nitrogen, the sorptive capacity may be renewed indefinitely.

BUFFERING. The pH is a critical factor in many reactions involving pollutants. Buffering is the resistance to a pH change of the soil solution. The basis of buffer capacity lies in the adsorbed cations on the exchange complex of the soil. The higher the exchange capacity, the greater will be the buffer capacity. The portion of the cation exchange capacity occupied by exchangeable bases is termed base saturation. There is a correlation between base saturation and pH, with higher base saturation for higher pH. The degree of buffering is lowest at the extremes of base saturation, and highest at intermediate base saturation values.

The extent of buffering in most cases will be relatively unimportant if the pH of the waste discharge is between 6 and 9. These pH values correspond to those commonly found in natural groundwater. Wastes with a pH in this range will generally be buffered to an extent that the percolating waste water will present no unusual problem. Consideration of buffering is thus of foremost importance in cases of disposal of very acidic or basic wastes. Detailed considerations are presented in Buckman and Brady (1969).

CHEMICAL PRECIPITATION. It is theoretically possible to precipitate almost any dissolved species from solution. However, in soil-groundwater systems, the necessary species often are not present in sufficient quantities to precipitate potential pollutants. Certain constituents are normally present and available for reaction in most groundwater, soil, and geologic materials. Calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, and silica are usually the major species in groundwater. Iron, aluminum, nitrogen, and carbonate, in addition to the previous constituents, may be found in soil and geologic materials.

There are important precipitation reactions for calcium, magnesium, bicarbonate, and sulfate. Calcite, aragonite, gypsum, and magnesium carbonates are major compounds which may precipitate in the soil and vadose zone. In arid areas, virtually all major constituents could be precipitated at or near the land surface in some situations; however, in this case virtually all of the waste has evaporated and percolation is minimal. The following trace constituents have important precipitation potential: arsenic, barium, cadmium, copper, fluoride, cyanide, iron, lead, mercury, molybdenum, zinc, and radium.

No rigorous procedure is given herein to evaluate chemical precipitation. However references such as Hem (1970), Stumm and Morgan (1970), Faust and Hunter (1967), and Gould (1967), detail thermodynamic calculations which may be used to evaluate this phenomenon. In many field situations data are commonly lacking on some parameters of importance, thus judgment is often necessary.

OXIDATION AND REDUCTION. The oxidation of organic matter in the topsoil is one of the most important pollutant attenuation mechanisms.

Oxidation and reduction reactions often work in conjunction with other mechanisms for pollutant attenuation. Besides those reactions causing precipitation, reducing conditions can also theoretically cause the formation of native elements such as arsenic, copper, mercury, selenium, silver, and lead, which are quite insoluble. Reducing environments can convert dissolved sulfate to sulfide and dissolved nitrate to nitrogen gas. Sulfides can react with certain metals to produce highly insoluble precipitates, such as sulfides of arsenic, cadmium, copper, iron, lead, mercury, molybdenum, nickel, silver, and zinc.

Oxidation and reduction reactions are also susceptible to analysis by thermodynamic considerations. These reactions are also subject to laboratory experimentation and no further detail is presented here.

VOLATILIZATION. Volatilization and loss as a gas can be effective for sulfate and nitrate. Mercury in solution can be volatilized in anaerobic environments or by reaction with dissolved humic acids. Several organic compounds of arsenic are volatile, and the escape of arsenic as a gas has been demonstrated for both aerobic and anaerobic soils. Selenium may be subject to volatilization, because of its chemical similarity to sulfur. The microbial reduction of nitrate to gaseous forms of nitrogen is well documented. No quantitative procedure is proposed to evaluate the extent of this phenomenon. It is more important to be aware of the pollutants that may be affected.

BIOLOGIC DEGRADATION AND ASSIMILATION. These processes are very important in the removal of organic and biologic pollutants. Many organic chemicals can be attenuated or removed by biological activity in the vadose zone. Sulfate, nitrate, arsenic, cyanide, mercury, and selenium are likely candidates for biologic fixation or volatilization. Molybdenum is strongly assimilated and concentrated by plants. Crop uptake can remove many of the nutrients in waste waters, particularly nitrogen, phosphorus, and potassium. However, the crop has to be removed or the pollutants may be introduced into the soil-groundwater system. Previous references, given under the step for identification of pollution sources and causes, contain relevant information as to evaluations of the extent of this phenomenon. Again, a general knowledge of the pollutants likely to be affected is of most use.

RADIOACTIVE DECAY. This mechanism is of great potential value in the attenuation of radioactive wastes by subsurface storage. Storage may be possible for thousands or tens of thousands of years, during which time the wastes would lose much of their activity through decay. Half-lives of many radionuclides are presented in references such as Davis and DeWiest (1966) and Hem (1970). The half-life represents the time required for a given quantity of the radionuclide to decay to one-half the original quantity. Consideration of this phenomenon is unnecessary for most cases of groundwater pollution monitoring, as radioactive pollutants are relatively uncommon.

In summary, attenuation above the water table is greatest for biological constituents. Many organic chemicals and trace elements and some radionuclides and inorganic chemicals will not generally reach the water table. The most mobile constituents would generally be the major inorganic chemical constituents and tritium. Chloride, nitrate, sulfate, sodium, and boron can be fairly mobile. Other major chemical constituents in the topsoil or vadose zone can be mobilized during waste disposal operations. Changes in pH, oxidation potential, and ion-exchange can cause this mobility. Potassium and phosphorus are ordinarily immobile in alluvial sediments, but could be mobile in flow-through consolidated rocks. Iron and manganese are often found in groundwater and are thus fairly mobile. Trace elements such as chromium, cadmium, arsenic, molybdenum, and selenium, which form anions in water, appear to be fairly mobile in some cases. Others such as barium, mercury, and cobalt are relatively immobile in most soil-groundwater systems. Some pesticides are mobile under certain conditions. Bacteriological pollutants are generally removed above the water table unless this zone is bypassed.

The evaluation of pollutant mobility above the water table requires considerable judgment on soils physics and chemistry, hydrogeology, and water chemistry. Such an evaluation is essential in order to accurately select what portion of the system should be monitored, and to what degree. This judgment may often require a team of specially trained investigators. Experience gained from case histories may be combined with this judgment to effectively perform this step.

Step 9 — Evaluate Attenuation of Pollutants in the Saturated Zone

Many of the attenuation processes which occur in the vadose zone can also occur below the water table, but in a modified manner. For example, the lower oxygen content below the water table reduces the possibility of oxidation of organic matter. Some pollutants, such as iron, may be more mobile in the reduced state. Reducing conditions are favorable, however, in some cases for pollutant removal from water, particularly for sulfate and nitrate. Another major consideration is that organic matter, common in the topsoil, is virtually absent in many types of geologic materials comprising the aquifer. This would ordinarily decrease the extent of sorption as well as reactions such as denitrification. In addition, certain geologic materials, such as granite or limestone, may lack many of the common substrates for sorption. The dilution process below the water table differs greatly from that operative in the vadose zone.

PROCESSES OTHER THAN DILUTION. The attenuation processes other than dilution do not generally have to be considered in detail if there is an adequate thickness of the vadose zone for treatment. In cases where the water table is shallow or a large part of the vadose zone is bypassed during waste disposal, detailed consideration of these processes may be necessary. Filtration and sorption are discussed in Step 8; however, in saturated flow, pollutant movement is generally horizontal. Thus, instead of utilizing a thickness of vadose zone beneath a waste disposal site, a volume of the aquifer is selected. Generally this will correspond to the projected volume and location of recharged waste water plume at a specific time. This volume can be estimated by utilizing flow net analysis to determine the vertical and horizontal direction of groundwater movement from beneath the waste disposal site. Specific distances from the waste discharge site, such as 100 feet, 500 feet, and 1000 feet, can be chosen and volumes of material calculated for each.

Buffering can be handled as discussed in Step 8. Generally, this is not of great concern unless extremely acidic or alkaline wastes are disposed of directly to the saturated zone, i. e., the vadose zone is bypassed. Chemical precipitation can be handled as described in Step 8. One major difference in this process compared to that occurring in the vadose zone is the general lack of evapotranspiration as a factor in concentrating solutions. In addition, the materials are continuously saturated below the water table and are usually not exposed to drying. Oxidation and reduction can be handled as discussed in Step 8. However, in the saturated case, oxidation is generally less important and reduction is more important than in the vadose zone. Volatilization and radioactive decay can be handled as discussed in Step 8.

DILUTION AND RELATED FACTORS. Once percolating wastes reach the zone of saturation, in most dynamic groundwater systems there will be a physical attenuation of pollutant concentrations with distance from the intersection with the water table. This attenuation is generally of much greater magnitude than that due to the previously discussed factors. This attenuation is one of the primary factors that mitigates against widespread groundwater pollution. In one sense, this restricted dilution is analogous to that of a plume of polluted air. The attenuation occurring in most cases is determined by the following factors:

- The volume of waste water reaching the water table
- The waste loading, i. e., the weight per unit area of pollutant reaching the water table
- Areal hydraulic head distribution, as indicated by water-level elevation contour maps
- Transmissivity of aquifer materials

- Vertical hydraulic head gradients and vertical permeabilities through confining beds which are present
- Quality of native groundwater in a three-dimensional sense
- Quantity of recharge reaching the water table from other sources at the land surface
- Quality of recharge reaching the water table from other sources
- Well construction
- Pumpage volumes and patterns.

The first two factors determine the concentration of pollutants reaching the water table. The third and fourth factors, along with porosity, determine the direction and magnitude of horizontal groundwater inflow and outflow from the area. The fifth factor determines the direction and magnitude of vertical groundwater flow in the area. The sixth factor comprises the quality of groundwater with which the recharged waste water will mix. The seventh and eighth factors determine the effect of recharge from other sources on pollutant concentration. Lastly, well construction can allow short-circuiting of aquifer materials and well pumping can drastically alter the hydraulic head distribution.

A first approximation of dilution can be obtained by assuming that the recharged waste enters a certain part of the aquifer; for example, the upper 10 feet, 50 feet, or 100 feet, over a certain area. Knowledge of the extent of groundwater pollution in historical situations in the area or a comparable area can be used to make this evaluation. Secondly, water reaching the water table from other sources of recharge and groundwater inflow from nearby areas usually tends to dilute the recharged wastewaters. The dilution can be calculated if the volume and quality of the various sources of water are known. Conservative constituents, such as chloride, can be used for a first approximation of dilution. In most cases, the pollutant of interest will be less mobile and thus occupy a smaller plume than a mobile constituent such as chloride. Groundwater outflow tends to carry pollutants away from the waste disposal site.

Water level elevation maps and flow nets can be used to consider whether the waste discharge is in an area of converging or diverging groundwater flow, which affects dilution. Vertical head gradients indicate whether wastes could move to deeper levels of the aquifer or whether deeper aquifer water could move up and dilute the wastes. Both cases tend to accentuate mixing or dilution. Aquifer transmissivity can be used to calculate groundwater flow rates into and out of an area. The quality of sources other than the waste discharge and native groundwater will obviously affect dilution as the lower concentration waters will exert relatively more dilution. The foregoing factors can be integrated into a mass balance analysis, both for the recharged wastewater and for the individual pollutants.

Wells affect dilution in several ways:

- Gravel packs or perforations in certain situations can act to short-circuit confining beds and allow vertical movement of pollutants near the well
- Well pumping can drastically alter flow patterns, both horizontally and vertically
- Well pumping can remove pollutants from groundwater and expose them to subsequent loss at the land surface or in the topsoil, by processes such as volatilization, crop uptake, and precipitation.

Most of these factors are significant for all types of pollutants that reach the water table, whether they are inorganic chemical, physical, organic chemical, bacteriological, or radiological. In some cases, certain factors do not attenuate the pollutant concentration, but rather increase it. An example is the development of a large depression cone in an agricultural area, whereby pollutants are drawn into the area from many directions but are effectively prohibited from leaving by the depression. The factors leading to attenuation or concentration of pollutant concentrations in the saturated zone have seldom been analyzed in case histories.

Plumes or zones of polluted groundwater may behave as a slow-moving viscous mass, but they may also be quite dynamic, especially where influenced by recharge and/or well pumping.

Evaluation of pollutant attenuation mechanisms in the saturated zone requires considerable hydrogeologic judgment. Such an evaluation is essential in order to properly determine the location and construction of monitor wells. Hydrogeologic judgment combined with experience gained from case histories may be effectively used to perform this step.

Step 10 — Prioritize Sources and Causes

The monitoring methodology presented thus far consists of a sequence of monitoring objectives or steps which must be performed in order to prioritize the identified sources and causes of groundwater pollution for monitoring within each of the selected monitoring areas. These monitoring objectives are presented not only in a chronologically preferred order for accomplishment but also occur in an order of increasing difficulty, both in terms of the monitoring methods available to accomplish these objectives and in terms of capability to interpret the data obtained from using these methods. Concomitantly the costs increase with implementation of these methods and the analytical procedures used in their evaluation.

In the early stages of a monitoring program it will not be possible to make an accurate prioritization of the pollution sources because of incomplete data and knowledge regarding the fate and transport of pollutants in site-specific situations, unless considerable monitoring is already underway. The prioritization scheme is dynamic in nature and with time will tend toward an optimum as more information is gained from a monitoring program.

Each objective of the methodology has been carefully selected to identify and build up the prioritization scheme which follows. In Step 1 criteria for selecting the monitoring areas are set forth. Step 2 prescribes that each monitoring area should be fully inventoried for known or potential sources and causes of groundwater pollution, and the method of waste disposal associated with each source determined. Completion of Step 3 will result in the identification of the biological, chemical, physical, and radiological characteristics of the pollutants associated with each source and as a result will allow a trial ranking to be made of the sources and causes in terms of the potential of the various pollutants to violate drinking water standards. Completion of Step 4, which has as its objective identification of groundwater usage in the vicinity of each source will allow a further refinement of the trial ranking of the sources and causes made in Step 3, based this time on their threat to existing groundwater usage.

The various uses of groundwater including the applicable water quality standards are discussed in Section III of this report under the heading Quality in Relation to Water Use. Of the possible uses of groundwater, it is apparent that usage for potable water supplies stands out as paramount. Therefore, sources and causes which pose a health threat to potable water supplies will have priority over nonhealth-related damages to potential users. Of foremost concern then in the prioritization will be pollution sources expected to result in the presence of pollutants exceeding the U. S. Public Health Service mandatory drinking water limits. For other sources of pollution the damage to users can be estimated on a monetary basis and the prioritization carried out based on the cost of anticipated damages to existing or potential users. The cost of groundwater quality degradation has been estimated, in areas such as the Los Angeles Basin in Southern California, in terms of the following considerations:

- Quality-related consumer costs, i. e., the cost of various treatments such as water softening or chlorination
- The cost of removing the pollutant to the background level of the groundwater resource
- The cost of removing the pollutant in the groundwater to the limits of drinking water standards.

In another instance a detailed investigation was made of an incident where a freshwater aquifer has been polluted by accepted disposal of oilfield brine through an "evaporation" pit and later a faulty disposal well (Fryberger, 1972). Several rehabilitation methods were evaluated in detail, including controlled pumping to the Red River and deep-well disposal. Although real economic damage both present and future resulted from this brine pollution, rehabilitation was determined to not be economically justified.

With completion of Steps 2, 3, and 4 of the methodology a much improved appreciation of the potential for groundwater quality degradation at the land surface will be realized.

One of the more difficult tasks facing a DMA charged with monitoring groundwater pollution sources will be to gain an accurate understanding of the fate and transport of pollutants associated with particular sources in site-specific situations. The presence of a pollutant at the land surface does not necessarily demonstrate a threat to groundwater quality. In most situations important data deficiencies will exist relative to pollutant mobility. The application of generalizations regarding the fate and transport of pollutants subsurface should be used with great care. Sometimes under tight budgetary constraints no other choice will exist. In such cases the application of rule of thumb generalizations should be left only to the specialist.

The objectives of Steps 5 and 6 are to gain a site-specific appreciation of the hydrogeology and existing water quality in relation to the pollution sources. In general, it will not be an objective of Steps 5 and 6 to require that regional appraisals of hydrogeology and groundwater quality be conducted, unless a diffuse source covering many square miles is involved. Regional appraisals of hydrogeology are outside the overall objective of the groundwater pollution monitoring methodology described in this report. This does not preclude that regional studies will be conducted by other agencies in cooperation with the DMA.

Steps 7, 8, and 9 comprise the basis for estimating pollutant mobilities and their ultimate presence at a point of groundwater discharge. Based on the estimations of pollutant mobilities determined as a result of the analyses carried out in these three steps, it will be possible to make a more accurate revision of the prioritization made in Step 4. The final three-phase adjustment in the prioritization will be made by considering first the potential pollutants at the land surface (Step 7), secondly, pollutants potentially reaching the water table (Step 8), and lastly, pollutants potentially reaching water supply wells (Step 9).

The refinement in the prioritization carried out as the result of Step 8 will have particular significance in terms of the nondegradation mandates of PL 92-500 and for the protection of sole source aquifers as required under PL 93-523. The refinement in the prioritization carried out as the result of Step 9 will have particular significance in demonstrating whether or not existing users are being threatened and for estimating potential damages to these users. Solute transport models will play an increasingly important role in the years to come as a means for estimating the damage potential to the groundwater users.

Prioritization of potential pollutants at the land surface (Step 7) will require an estimation of the annual volume of liquid waste or weight of solid waste subject to leaching, pollutant concentration, solid or liquid waste loading per unit area, and pollutant loading per unit area.

Completion of the procedural steps and resulting prioritization scheme suggested above will allow a DMA to direct its monitoring resources in a most effective manner toward the primary goals of PL 92-500 and PL 93-523. The prioritization obtained will need to be reevaluated on at least a yearly basis as pollution controls are implemented and as new sources of pollution are detected.

Step 11 — Evaluate Existing Monitoring Programs

Every effort should be made to incorporate these ongoing activities in a new monitoring program. In fact, such inclusion is essential if the program is to be both comprehensive and cost-effective.

Existing monitoring activities in an area may be carried on by the following agencies or organizations:

- U. S. Geological Survey — groundwater and surface water quality data
- State geologic and water agencies — groundwater and surface water quality data
- Local water districts (flood control, irrigation, water conservation, etc) — groundwater and surface water quality data
- Health departments (city, county, and State) — data on quality of groundwater from water supply wells
- Sanitation districts — data on quality of treated waste water effluent before disposal on land
- Industries — data on quality of self-supplied groundwater and of treated waste water effluent before disposal on land
- Local consulting firms working in the water resources field.

It should be noted that many of the existing monitoring programs are not specifically oriented toward monitoring groundwater pollution. Thus, their value is often limited. With the review of existing monitoring programs completed, it will be possible to determine monitoring deficiencies. This is accomplished by noting the availability of existing monitoring activities serving the high priority sources and causes. Clearly, if the surveillance systems for these are inadequate or incomplete, monitoring deficiencies exist.

The final result of this step will be a priority listing of sources and causes having monitoring deficiencies. The sequence of this listing will be identical to that developed in Step 10, except that sources which are adequately monitored will be eliminated from the list.

Step 12 — Establish Alternative Monitoring Approaches

As a result of making a first pass through the first 11 steps of the methodology a DMA will have a good appreciation of those sources and causes of groundwater pollution which hold the highest priority for monitoring. Although in some cases the accuracy of this first-cut prioritization will be questionable, an important objective will have been accomplished — that of identifying data and information deficiencies.

In Step 11 the existing monitoring programs were checked to ascertain if it would be possible to modify these existing monitoring activities to collect the needed data. Whether or not this can be accomplished will usually be determined on legal or institutional grounds. In some instances it may be a least-cost approach to pay to have specific data collected during the course of ongoing monitoring programs.

Based on the data and information deficiencies identified in the prioritization of Step 10, it will be possible to identify the required alternative monitoring approaches. To establish the alternative monitoring approaches it will be necessary to first identify and develop pollutant-specific technical monitoring objectives for the pollutants known to emanate from each source. For example, consider a landfill producing leachate high in dissolved solids. A pollutant-specific technical monitoring objective could be to determine total dissolved solids (TDS). A first step would then be to identify the monitoring zone (surface, vadose, or saturated zone), the monitoring methods that could be used to monitor TDS in each zone, the sample analysis techniques for each monitoring method, and sampling frequencies.

Since it is possible to have several combinations of monitoring zones, monitoring methods, sample analyses, and sample frequencies to meet the same technical objective, more than one monitoring approach may exist for each technical objective. By definition, a monitoring approach consists of a mix of monitoring methods. If only one method is feasible for meeting the technical objective, it follows that this method will be the preferred monitoring approach. When several monitoring approaches exist it will be necessary to make a cost-effective comparison between them in order to select the preferred approach.

SELECTION OF PORTION OF SYSTEM TO BE MONITORED. The portion or portions of the system to be monitored for each source depends on the method of waste disposal, infiltration potential, travel time of waste waters from the land surface to the water table, and the mobility of pollutants in the topsoil and vadose zone. Obviously, no monitoring is required in the topsoil or vadose zone if they are bypassed during waste disposal. If pollutants undergo significant attenuation above the water table, little monitoring may be necessary in the saturated zone. For example, in the case of phosphorus, which is readily adsorbed on soil particles, little monitoring in the saturated zone would be necessary for most diffuse sources. However, where overloading may occur, such as at point sources of wastes with a high phosphorus concentration, monitoring in the zone of saturation would often be necessary. In cases where significant storage capacity exists in the vadose zone and travel times of pollutants to the water table are long (decades or centuries), sampling in the vadose zone may be stressed. Likewise, in cases where waste water application and infiltration rates are very small (several millimeters per year), monitoring in the vadose zone may be emphasized.

In cases where there is rapid movement through the vadose zone and high waste water application and infiltration rates (tens or hundreds of feet per year), sampling in the vadose zone is minimal and water well sampling is maximal. Where sources are highly variable in potential pollutant composition or in cases where the composition is poorly known, intense source sampling may be necessary. In cases where the composition is fairly constant or relatively well known, little source sampling may be required. Selection of the portion or portions of the system to be monitored requires judgment on the soils, hydrogeology, and water chemistry.

It is also necessary to determine the area over which to sample. This is self-explanatory for land surface monitoring. In the case of the vadose zone, generally, sampling can be confined to the area beneath the pollution source. This is particularly true in cases where geologic materials allow primarily vertical movement to the water table. In cases where layers of low permeability inhibit vertical flow, significant lateral flow may take place. If this factor is predominant, sampling in parts of the vadose zone only under the source of pollution may be ineffective. In this case sampling of a much larger area may be warranted, and batteries of piezometers and tensiometers may be necessary to determine this area.

In the saturated zone, the area to sample depends largely on pollutant attenuation factors in the aquifer. These factors have been discussed previously in Step 9 of the methodology. Application of the methodology of Step 9 will allow estimation of the horizontal extent of pollutant travel in the aquifer.

SELECTION OF NONSAMPLING METHODS. Nonsampling methods at the land surface almost always will include the waste load inventory. The testing of liners, pipelines, and tanks for leakage is obviously only applicable to cases where the type of waste disposal involves these items. Aerial surveillance is generally useful when sources of pollution methods of waste disposal are poorly known or when the method of waste disposal is highly variable. Nonsampling methods in the vadose zone largely comprise in-place measurements of moisture characteristics, such as by neutron logging, tensiometers, and moisture blocks. These methods are most useful for point sources of pollution. Experienced soils scientists and hydrologists can best select the appropriate tool. In the saturated zone, most nonsampling methods are of direct use only in special cases, for example, resistivity surveys which are generally applicable only to cases of high salinity waste disposal.

DETERMINATION OF SAMPLING PROCEDURES. A determination must be made of the required sampling in each portion of the system, namely the land surface, the topsoil and vadose zone, and the saturated zone. This sampling primarily involves liquids and solids. Solids at the land surface comprise stockpiles and other items subject to leaching. Solids in the subsurface comprise soils and geologic materials. The liquids at the land surface are primarily waste waters or polluted surface water. Liquids to be sampled in the subsurface include native waters and polluted waters.

The determination of the required sampling is based on what data are already available, the purpose of monitoring, the type of pollution source and pollutants, and the method of waste disposal. This probably requires more judgment relative to soils and hydrogeology than any other part of the monitoring methodology. Sampling of solids at the land surface is often unnecessary if the composition is generally known. An exception would be the radium content in byproduct gypsum from phosphorus fertilizer production, especially if this content is not well known or is highly variable. In general, waste waters of highly variable composition (many industrial wastes) will require much more sampling than those of more consistent composition (many municipal wastes). As an example, the composition of septic tank effluent is generally well known if the composition of the water source is known. Sampling of waste waters in the case of toxic materials and highly variable composition is a major tool in monitoring groundwater pollution.

In the topsoil and vadose zone, the tools required to retrieve water and soil samples will vary greatly with geographic area due to differences in soil, geological, and climatic conditions. In many situations, the type of augering or drilling depends highly on the nature of subsurface deposits, the moisture characteristics, and the depth of exploration. The specific reason for monitoring and pollutants to be monitored often dictate the tools for sample retrieval. For example, moisture cups may have important limitations with regard to bacteriological sampling. Many of the limitations of specific sampling devices have been discussed by Everett et al. (1976).

In the case of the saturated zone, significant data may be obtained by sampling existing wells, tile drains, springs, and baseflow of streams. For wells with fixed pumps, water samples may be taken directly from the well discharge if it is freely discharging or a faucet or other opening is provided. In the case of wells without pumps, submersible pumps may be installed. Open wells can be sampled by a number of down-the-hole devices. The determination of which wells to sample, and the extent of additional test wells that need to be drilled depends on the purpose of monitoring, aquifer characteristics, and mobility of pollutants in the aquifer. The portion of the aquifer to be monitored must be determined; for example, the upper 10 feet, the lower 50 feet, or a composite of the entire aquifer. The construction of monitor wells requires consideration of subsurface geology, aquifer characteristics, and hydraulic head distribution. In local areas well construction techniques must be determined by persons experienced in the area. Down-the-hole sampling generally supplies a sample representative of a very small area in the aquifer. Small-capacity wells pumped for short time periods also reflect fairly local conditions. High-capacity wells pumped for long time periods can indicate regional conditions and integrate quality data over large areas.

DETERMINATION OF REQUIRED ANALYSES. The pollutants in the major sources have been previously described. For the determination of required analyses, consideration is given to liquid wastes, solid wastes, soil and geologic materials, and water in the soil-groundwater system.

Liquid Wastes. In general, the analyses of liquid wastes can be based on known compositions from the literature. Specific parameters of importance to groundwater pollution can be selected. In general, the more mobile constituents would have priority, as well as those of greatest importance in subsequent reuse of polluted water. There are great advantages to running relatively complete chemical analysis for the major species commonly found in groundwater, namely calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, sulfate, nitrate, and silica. Electrical conductivity, total dissolved solids, and pH are also routinely determined. With the determination of other major ionic species in polluted waters, such as ammonium and fluoride, certain procedures can be used to check the chemical analyses. Determination of these parameters also allows for limited chemical equilibrium calculations. In case of a drinking water supply, fluoride and arsenic would also be important parameters. For agricultural supply, boron would also be important. Some of the more common trace elements in polluted groundwater are arsenic, chromium, cadmium, molybdenum, iron, and manganese. With respect to nitrogen, phosphorus, and sulfur, various forms may have to be determined, such as ammonia, organic nitrogen, nitrite, and nitrate in the case of nitrogen. Oxidation potential is also important in this case.

Electrical conductivity monitored on a regular basis can be used as an indicator for concentration changes in major constituents. Monitoring for total salinity in salt balance studies may only require determination of electrical conductivity. Another widely used measurement is chloride content. Chloride is common in many types of liquid waste, is extremely mobile in the soil-groundwater system, and is therefore of special value as a tracer. Representative constituents of interest in groundwater pollution are given by Everett et al. (1976). If wastes have certain characteristics and insufficient attenuation occurs, secondary effects of crucial importance to groundwater pollution monitoring could result. For example, acidic wastes, which if not buffered sufficiently above the water table, could mobilize certain trace elements in minerals in the aquifer.

Bacteriological determinations are not generally of great importance in waste water, unless specific pollutants have been found in groundwater near a pollution source. The bacteriological composition of most waste waters is generally known from the literature. Radiological determinations are very important in selected cases. The composition of organic chemicals possibly entering groundwater could assume a major role in the future. At present most organic chemicals are generally known and will rarely have to be sampled in waste liquids. Again if a problem is found in well samples, a specific pollutant may need to be monitored in waste waters.

Solid Wastes. Analyses to be run on solid wastes are highly variable. In general, the major chemical constituents are well known from the literature (for example, gypsum stockpiles). Thus analyses usually focus on trace element content and radioactivity.

Soil and Geologic Materials. The physical analyses on soil are generally performed in order to monitor moisture characteristics and water movement in the vadose zone. The selection of these parameters is based on soil and hydrogeologic judgment. Chemical analyses will generally be limited to materials absorbed on or precipitated in the materials. Trace elements and radionuclides would be commonly analyzed. Trace elements and radionuclides in geologic materials which might be mobilized by disposal of certain toxic wastes may also be analyzed.

Water. In general, the analyses for water in the vadose zone and aquifer are related to those for waste water at the land surface. However, analyses of wastes at the land surface can considerably narrow down the required analyses for water beneath the land surface. The relative immobility of some pollutants in the topsoil often renders analysis of water for these constituents in the vadose zone unnecessary. For example, many bacteriological constituents and trace elements can be removed in the topsoil under a favorable set of circumstances. Sampling in the vadose zone indicates additional attenuation of pollutants. Thus, in most respects, analyses for aquifer water may require the least determinations, since many potential pollutants will not reach the aquifer. In any case, the major inorganic species commonly found in groundwater should generally be determined. This is primarily for the sake of checking chemical analyses, equilibrium calculations, and providing data for the use of trilinear diagrams and other analytical tools.

Generally in the early part of a monitoring program, sampling for detailed determinations is made. This decision is based on the knowledge of trace elements, radionuclides, bacteriological constituents, and organic chemicals in the aquifer of the selected area. In general, nationwide, there is a dearth of data on these substances. The substances of major concern will be elucidated by source monitoring, and secondarily by monitoring in the topsoil and vadose zone.

DETERMINATION OF SAMPLING FREQUENCIES. The selection of sampling frequencies often involves a trial and error procedure. In general, the fluctuations with time in composition over short periods (days or weeks) are greatest for waste water at the land surface and least for groundwater samples. In general, passage of pollutants through the topsoil and vadose zone will tend to smooth out fluctuations in composition at the land surface. In sampling at the land surface, the foregoing should be kept in mind. Often the extremes in concentration are not desired, but rather an integrated or typical value. For waste water sampling, open pond water subject to mixing processes can often be sampled monthly to determine the major characteristics. Compositing may be advisable, but is usually done on the waste stream. A trial and error procedure is often used, and the main idea is to establish seasonal changes or patterns in quality. Chemical hydrographs can be plotted and used as an aid in selection of optimal sampling frequencies.

Geologic and soil samples are generally analyzed less frequently than waters. In many cases geologic sampling may only be done once. Easily retrievable soils samples (upper 5 to 10 feet) may be analyzed several times a year or annually. Water in the vadose zone in areas of rapid percolation should generally be done monthly or quarterly. The frequency of sampling in this case is limited by the slowness of water movement into sampling devices. In areas of slow percolation to the water table, measurements may be made only every 5 or 10 years.

Water samples in the aquifer can often be collected on a semiannual basis for large-capacity wells once seasonal trends are established. In the early part of sampling programs, analyses on a weekly, daily, hourly, or more frequent schedule may be necessary. In cases of point sources, monthly analyses may be necessary. For diffuse sources, annual sampling of wells pumping long time periods will generally suffice, but only when seasonal trends have been established. For low-capacity wells, more frequent sampling of a greater number of wells is necessary, and monthly sampling may be necessary in many cases. Chemical hydrographs can also be used in this case as an aid in selection of optimal sampling frequencies.

Specific examples which illustrate the selection and application of alternative monitoring approaches using the stepwise procedure outlined in this report are given in Section II of a companion report in this series entitled Monitoring Groundwater Quality: Illustrative Examples (Tinlin, 1976).

Step 13 — Select and Implement the Monitoring Program

In Step 12 a procedure for developing pollutant-specific preferred monitoring approaches based on cost-effectiveness was discussed. When working with a source containing many pollutants it will not be unusual to go through several suboptimizations before a source-specific preferred monitoring approach can be selected. By definition, a source-specific preferred monitoring approach consists of the set of pollutant-specific monitoring approaches. The reason for this suboptimization is that in many cases it will be possible to measure more than one pollutant using the same method. The normal procedure when dealing with several pollutants from a single source will be to examine each in terms of the available methods for sampling and analyses and select the one best suited.

After a source-specific preferred monitoring approach has been selected for the highest priority source, the cost of implementing this monitoring approach will need to be computed and compared against the monitoring budget. If funds remain, the procedure for selecting a source-specific preferred approach and its implementation will be repeated for the next highest priority source and so on to each lower priority source until the budget is depleted.

A preferred monitoring program will consist of the set of selected source-specific preferred monitoring approaches. Monitoring approaches, e.g., remote sensing, which provide information pertaining to more than one source may assist in achieving cost-effectiveness at the program level. Certain other economies of scale will also exist at the program level when discounts for materials and chemical analyses are available and by spreading the cost of personnel and equipment over many sources.

The principal action in implementing a monitoring program for an area by a DMA will be to see that the necessary monitoring activities are carried out. This will involve making personnel assignments, purchasing monitoring equipment and data handling supplies, and letting contracts for services, such as drilling, performing well tests, and performing chemical analyses. A most important action on the part of a DMA will be to insure that a strong quality assurance program is carried out. A key consideration in this program will relate to a capability by the DMA to provide valid data to support enforcement actions in situations where environmental harm is projected.

It is important to recognize that additional monitoring may not imply large expenditures. Innovative techniques may produce useful quality data at low cost. For example, consider a large sanitary landfill, which potentially could be a major pollution source, that is not being monitored. If the DMA decides that monitoring of this source is important, then the first move should be to search for existing wells near and on the downgradient side of the landfill. Assume that three wells — two domestic and one irrigation — are found which satisfy the locational conditions. The appropriate action then would be for the DMA to arrange for regular sampling and analysis of the three well waters. If no wells were available then a more expensive alternative would be to drill one or more monitoring wells.

A data management system applicable to groundwater quality is described in a companion report, Monitoring Groundwater Quality: Data Management (Hampton, 1976). The selection of a system for a given area requires consideration of several factors. One is the volume of data to be handled by the system. A second is the use and distribution that will be made of the data. Third, the compatibility of a system with others that may be in use in the area must be considered. Fourth, decisions may already have been made at a higher administrative level, such as by a State, which will specify the monitoring system to be employed. And fifth, the cost of the system is an important factor. In general, where the monitoring program is small, as in an undeveloped rural area, the data management system can be extremely simple — perhaps only xeroxing and filing of a few data sheets. But in a large urban area which is heavily pumped, a sophisticated system involving digital computers may be essential to handling the input of monitoring data.

Step 14 — Review and Interpret Monitoring Results

A key function of a DMA after the implementation of a monitoring program is underway will be to collect and to review all current monitoring data in its area. The data should be analyzed and interpreted so as to define quality trends, new pollution problems, regions of improvement, and effectiveness of pollution control activities. Assessments such as those portions of the groundwater resource not meeting water quality standards and predictions of future quality under projected population and land use conditions should be prepared.

The responsibility of analyzing monitoring data to convert it to water quality information will be a continuing activity for a DMA. As new data are received, they should be studied promptly in order to detect changes rapidly, particularly those requiring immediate attention or action.

Step 15 — Summarize and Transmit Monitoring Information

The final result of a monitoring program organized in an area by a DMA is information on groundwater quality. Thus, the final task of a DMA is to disseminate the information gained in usable forms to the agencies and organizations concerned with such information.

Monitoring should be summarized in appropriate forms for convenient study before distribution outside of the DMA. This may involve preparation of tables showing averages and/or changes in water quality. Similarly, graphs prepared to readily display long-term trends may be helpful. Maps showing, for example, locations of major known sources of pollution, areal distributions of concentrations of key pollutants, and regions having groundwater with qualities not meeting drinking water standards, can also be shown to be both useful and effective.

Monitoring information should be distributed regularly to appropriate public agencies — local, State, and Federal. Major industries in the area should also receive the material as well as cooperating agencies and organizations that contribute monitoring data. In addition, the general public should be informed of the results of the monitoring program; therefore, reports should be sent to local newspapers, citizens' groups, Chambers of Commerce, and conservation and environmental organizations. It can be expected that the public awareness of groundwater quality created by such publicity efforts will indirectly act to encourage individuals and organizations to preserve and to protect the underground resource which they, perhaps for the first time, more fully understand.

Finally, a DMA has the responsibility to alert action and enforcement agencies of critical problems or situations which are discovered within the monitoring program. This may involve, for example, detection of hazardous or toxic pollutants which could imminently affect a nearby municipal well field. Prompt reporting of such instances is essential as well as following up with specialized monitoring efforts for documenting and controlling emergency situations.

EXAMPLE 1 — TABULAR PRESENTATION OF GROUNDWATER QUALITY. Table 5 illustrates a format for presenting groundwater quality data in tabular form. With the exception of temperature, only chemical quality data are included. Note that the ionic constituents are presented both in milligrams per liter and milliequivalents per liter and that hardness includes both total and noncarbonate values. The well-numbering system is based on township and range designations so that the well location is known from the table to the nearest quarter-quarter section. In this table some wells have been sampled semiannually in the spring (for high groundwater level conditions) and in the fall (for low groundwater conditions), while others have been sampled only once a year.

EXAMPLE 2 — GRAPHICAL PRESENTATION OF GROUNDWATER QUALITY. Graphical representations of analyses of the chemical quality of groundwater are useful for display purposes, for comparing analyses, and for emphasizing similarities and differences. Graphs can also aid in detecting the mixing of waters of different composition and in identifying chemical processes occurring as groundwater moves through the underground. A variety of graphical techniques is available; some of the more useful ones are described and illustrated in the following paragraphs.

Figure 8 illustrates the most widely used bar graph in the United States. Each analysis appears as a vertical bar graph whose total height is

TABLE 5. ANALYSES OF CHEMICAL QUALITY OF GROUNDWATER PRESENTED IN TABULAR FORM
(California Department of Water Resources, December 1974)

Owner and Use Sources; State Well and Other Numbers; Dates Sampled	Temp (°F)	Specific Conductance (micromhos at 25°C)	Mineral Constituents in mg/l													Total Dissolved Solids (ppm)	Sodium (%)	Hardness as $CaCO_3$		Analyzed by
			pH	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Carbonate (CO_3)	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)	Nitrate (NO_3)	Fluoride (F)	Boron (B)	Silica (SiO_2)			Total ppm	NC ppm	
TIA JUANA VALLEY BASIN (9-19)																				
Calif. Water and Telephone Co. 18S/2W-32H1 4-11-60	70	9852	7.3	504 25.15	292 24.05	1266 55.07	8 0.20	0 0.00	544 8.93	663 13.81	2870 80.93	5 0.09	1.0 0.05	0.72	32	7220	53	2160		DWR
11-15-60	70	13780	7.3	626 31.25	375 30.75	1870 81.30	2.5 0.06	0 0.00	528 8.65	506 10.54	4290 121.00	0 0.00	0.5 0.03	1.26	19	9630	57	3100	2667	Lein
18S/2W-32P4 4-11-60	69	22860	7.3	608 30.34	707 58.16	3710 161.40	90 2.30	0 0.00	2.96 4.86	1017 21.18	7900 222.80	9 0.14	1.0 0.05	0.83	30	16320	64	4425		DWR
11-14-60	68	23180	7.3	661 30.34	654 53.75	3850 167.45	108 2.77	0 0.00	303 4.96	1104 22.98	7890 222.50	0 0.00	0.4 0.02	1.16	19	15618	65	4338	4090	Lein
19S/2W-4A5 4-12-60	68	1965	7.6					0 0.00	326 5.35		402 11.35							510	242	DWR
12-6-60	66	2007	7.6					0 0.00	303 4.96		408 11.51							491	243	DWR
19S/2W-5O6 4-12-60	71	22260	7.0	680 33.93	681 56.07	3630 157.90	24 0.61	0 0.00	300 4.96	1075 22.40	7700 217.10	7 0.11	0.7 0.04	0.66	28	16250	64	4500		DWR
11-14-60	70	20780	6.7	714 35.63	573 47.09	3690 160.50	29 0.74	0 0.00	293 4.80	1066 22.20	7700 217.10	26 0.42	1.1 0.06	0.69	19	15692	66	4136	3896	DWR
Henry Schaffner 18S/2W-35L1 4-12-60		3830	7.6					0 0.00	567 9.30	1326 37.40								1245		DWR
12-6-60		2829	7.5	131 6.54	52 4.27	430 18.71	5.6 0.14	0 0.00	368 6.04	214 4.46	678 19.12	2.5 0.04	0.58 0.03	0.48	28	1740	63	540	23[illegible]	DWR
19S/2W-2E1 4-12-60		2550	7.6	226 11.30	87 7.15	589 25.60	9.4 0.24	0 0.00	424 6.94	455 9.48	909 25.65	57 0.92	1.2 0.06	0.53	16	2650	58	923	575	DWR
Aballo and Wright 19S/2W-3A1 4-12-60		2130	7.7	187 9.35	80 6.55	370 16.10	7.8 0.20	0 0.00	339 5.55	309 6.44	709 20.00	6.2 0.10	1.0 0.05	0.14	22	1424	50	795	517	DWR
Knox Dairy Farm 19S/2W-5G18 4-12-60	71	7072	7.5	328 16.37	190 15.63	955 41.54	5.6 0.14	0 0.00	405 6.64	472 9.83	1980 55.84	14 0.23	0.96 0.05	0.62	24	4967	56	1600		DWR
11-15-60	70	7210	7.0	406 20.25	157 12.85	975 42.40	2.5 0.06	0 0.00	387 6.35	845 17.61	1915 54.00	0 0.00	0.6 0.03	0.66	19	5390	56	1655		Lein

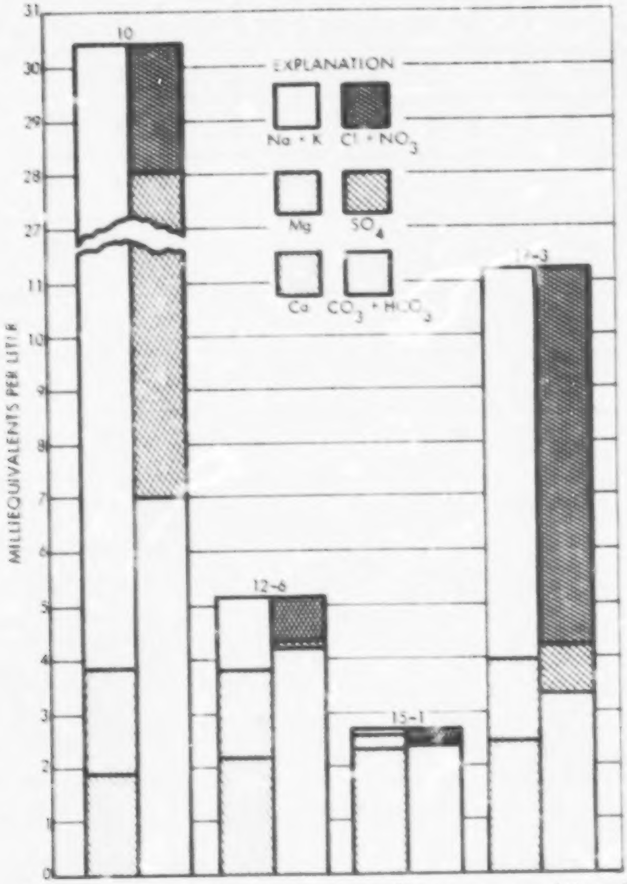


Figure 8. Vertical bar graph of chemical quality expressed in milliequivalents per liter (Hem, 1970).

proportional to the total concentration of anions or cations, expressed in milliequivalents per liter. The left half of the bar represents cations and the right half anions. These segments are divided horizontally to show the concentrations of major ions or groups of closely related ions, which are shown by distinctive patterns. Numbers at the tops of the bars serve to identify the analyses.

Figure 9 shows the same bar graph as Figure 8 but with addition of a bar for hardness. Values of hardness are expressed in milligrams per liter as $CaCO_3$, which is equivalent to the sum of the calcium and magnesium segments, in milliequivalents per liter, multiplied by 50.

Figure 10 also shows the same bar graph as Figure 8 but with the addition of a horizontal bar for silica. Here the concentration of silica is given in millimoles per liter because milliequivalents cannot be used for uncharged solutes.

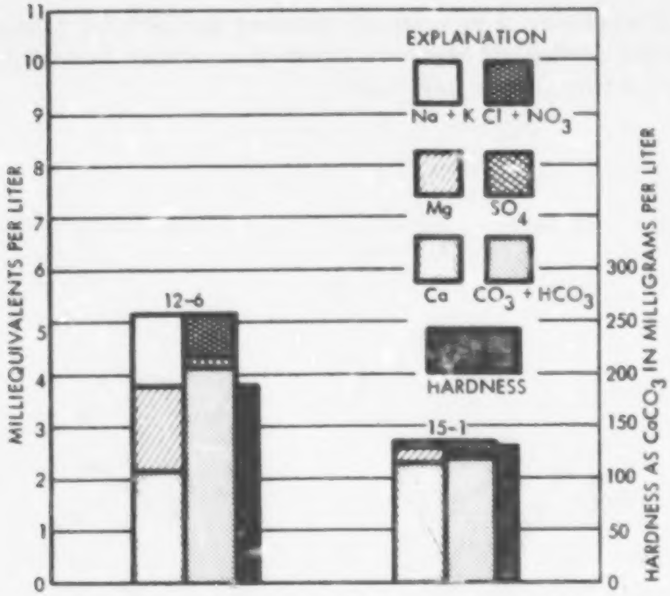


Figure 9. Vertical bar graph of chemical quality expressed in milliequivalents per liter which also shows hardness as $CaCO_3$ in milligrams per liter (Hem, 1970).

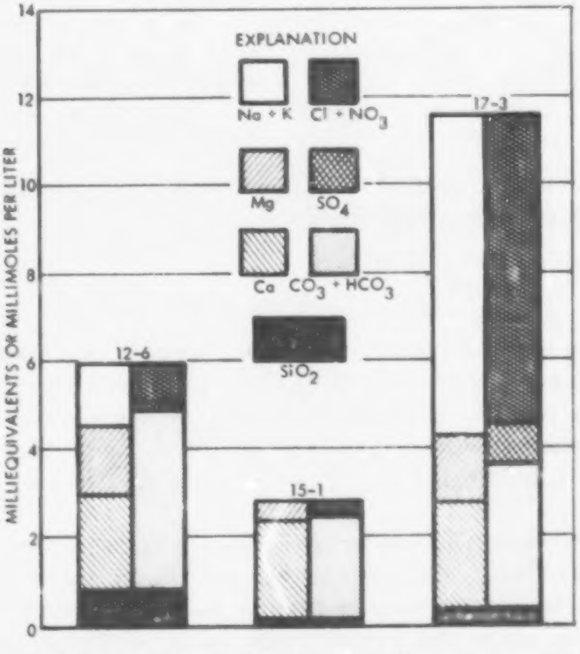


Figure 10. Vertical bar graph of chemical quality expressed in milliequivalents per liter which also shows silica in millimoles per liter (Hem, 1970).

Figure 11 illustrates a system of plotting quality by radiating vectors in which the lengths of the six vectors from the center represent ionic concentrations in milliequivalents per liter.

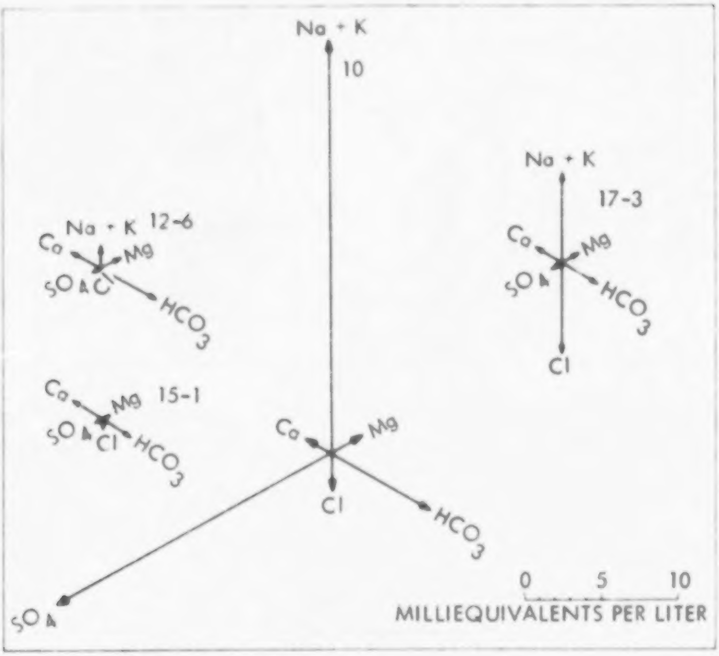

Na + K
10
Na + K
17-3
Ca
Mg
SO4
HCO3
Cl
Na + K 12-6
Ca
Mg
SO4
Cl
HCO3
Ca
Mg 15-1
SO4
Cl
HCO3
Ca
Mg
Cl
HCO3
SO4
0 5 10
MILLIEQUIVALENTS PER LITER

Figure 11. Radial vector diagram of chemical quality expressed in milliequivalents per liter (Hem, 1970).

Figure 12 shows a method for presenting analyses using four parallel axes extending on each side of a vertical zero axis. Concentrations of cations are plotted to the left and anions to the right, all in milliequivalents per liter. The resulting points are connected to form an irregular polygonal pattern; waters of similar quality define a distinctive shape.

Figure 13 indicates still another graphical representation of water quality. Here a circular "pie" diagram is drawn with a scale for the radii which makes the area of the circle represent the total ionic concentration. Subdivisions of the area show the proportions of the different ions as percentages of the total milliequivalents per liter.

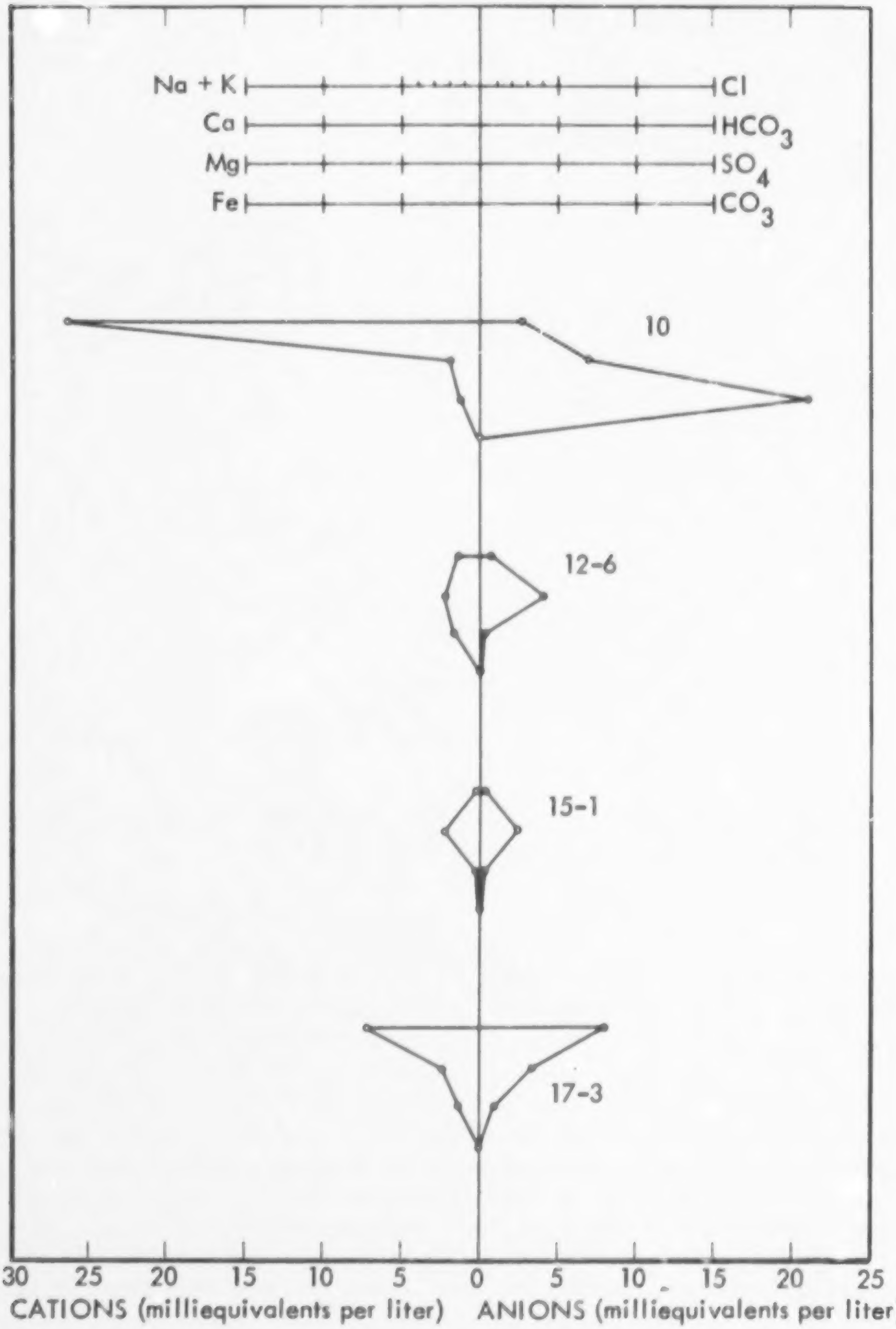


Figure 12. Pattern diagram of chemical quality expressed in milliequivalents per liter (Hem, 1970).

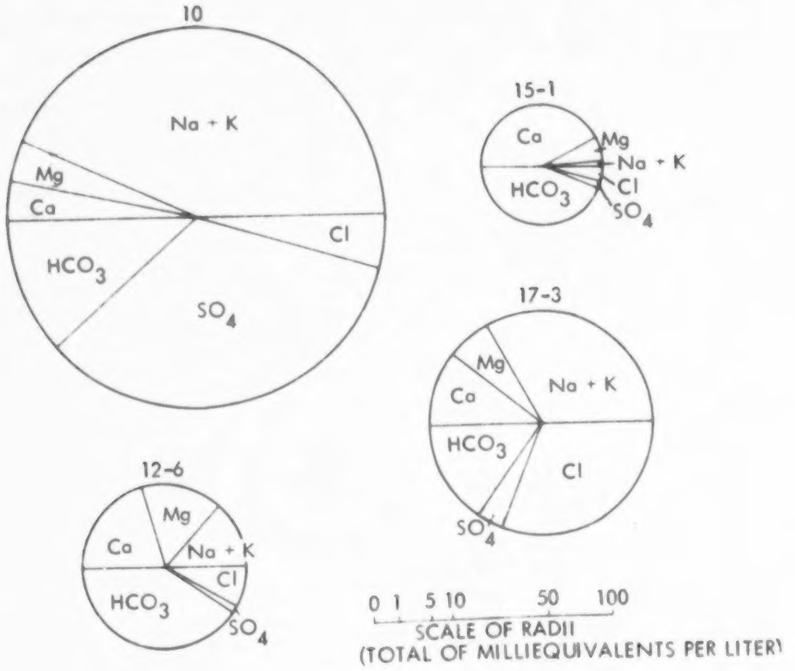


Figure 13. Circular diagram of chemical quality with subdivisions showing percentages of total milliequivalents per liter (Hem, 1970).

Figure 14 illustrates a trilinear diagram, which is a useful method for representing and comparing water quality analyses. Here cations, expressed in percentage of total cations as milliequivalents per liter, plot as a single point on the left triangle; while anions, similarly expressed as a percentage of total anions, appear as a point in the right triangle. These points are then projected into the central diamond-shaped area parallel to the upper edges of the central area. This single point is thus uniquely related to the total ionic quality, and at this point a circle can be drawn with an area proportional to the total dissolved solids concentration. The trilinear diagram is a convenient way to distinguish similarities and differences among various groundwater samples as waters with similar qualities will tend to plot together as groups. Also, simple mixtures of waters can be identified; for example, an analysis of any mixture of waters A and B will plot on the straight line AB on the diagram, where A and B are the analyses of the two component waters.

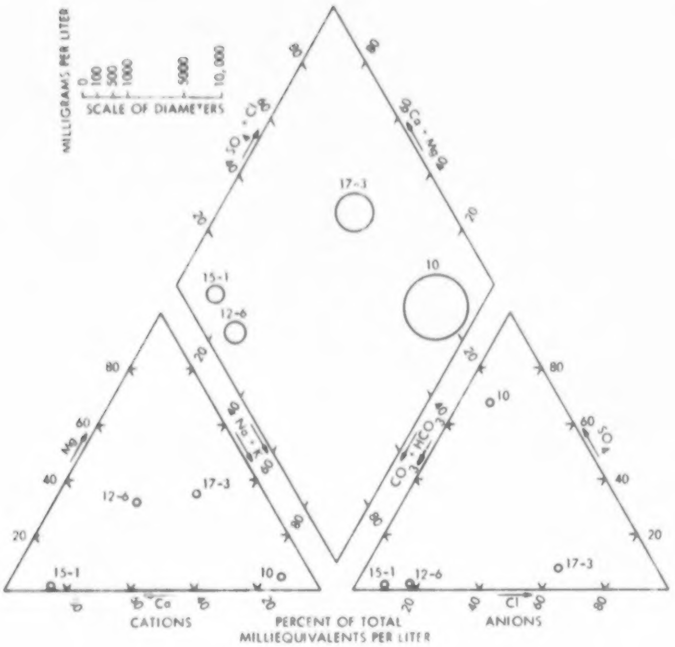


Figure 14. Trilinear diagram of chemical quality expressed in percentages of cations and anions as milliequivalents per liter and represented by two points and a circle (Hem, 1970).

Figure 15 is modification of the trilinear diagram which is convenient where a large number of analyses are to be graphically displayed. The triangle and diamond areas are the same as in Figure 14 except that they are shifted in position. The difference is that analyses are shown as points rather than circles on the diamond area and total dissolved solids are plotted to the right on a parallelogram with a logarithmic scale. In addition, hardness as $CaCO_3$ is plotted on a second parallelogram to the right of the cation triangle.

EXAMPLE 3 — QUALITY VARIATION WITH TIME. Figure 16 shows graphically the variation in chloride concentration with time for groundwater at Burlington, Massachusetts. The increase in chlorides is associated with the advent of road salting in the area. Salt was first stored uncovered in 1961, approximately 400 feet upgradient from the town's well field. At that

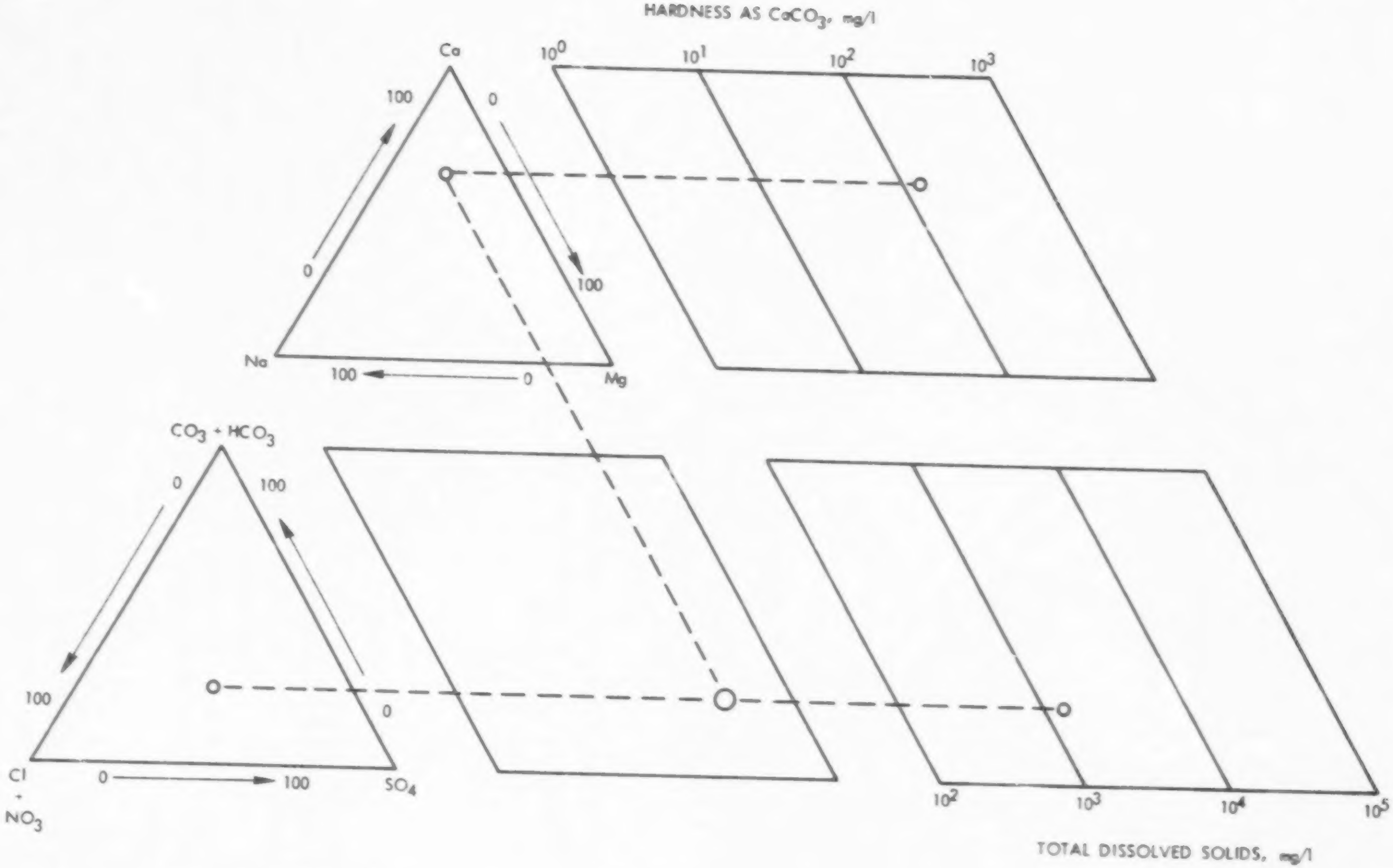

HARDNESS AS $CaCO_3$, mg/l
Ca
100
0
0
100
Na
100
0
Mg
10^0
10^1
10^2
10^3
$CO_3 + HCO_3$
0
100
100
0
Cl + NO_3
0
100
SO_4
10^2
10^3
10^4
10^5
TOTAL DISSOLVED SOLIDS, mg/l

Figure 15. Comprehensive trilinear diagram of chemical quality in which five points represent the proportions of cations and anions together with total dissolved solids in milligrams per liter and hardness as $CaCO_3$ in milligrams per liter.

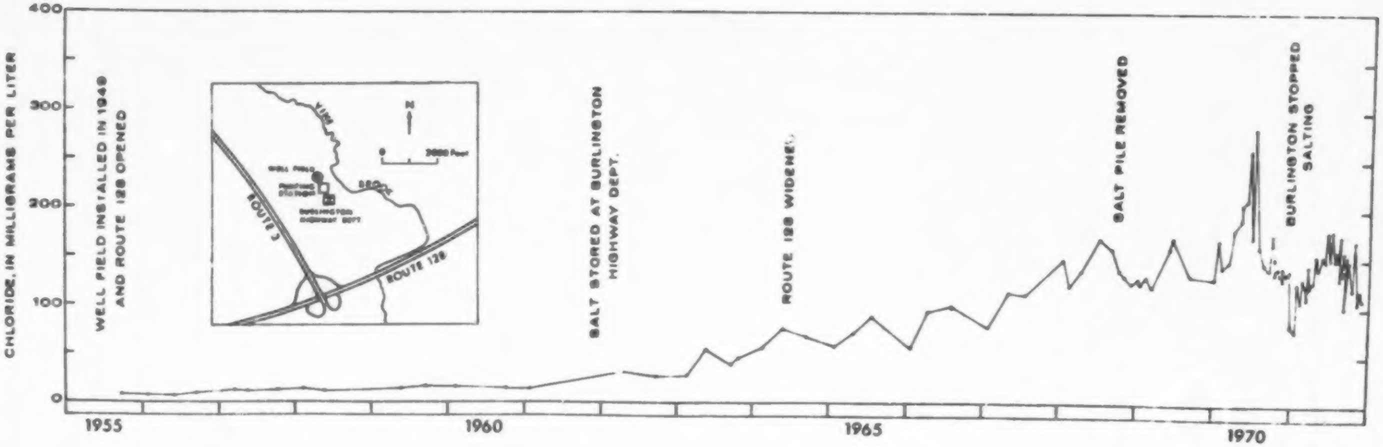


Figure 16. Variation in chloride concentration with time for groundwater at Burlington, Massachusetts (Terry, 1974).

time the chloride concentration was less than 15 mg/l; by 1963 the concentration began to increase notably. Remedial measures by Burlington included construction of a salt-storage shelter in 1968, when the chloride reached 170 mg/l, and banning the use of deicing chemicals on city streets in 1970, when the concentration exceeded the 250 mg/l upper limit recommended by the U. S. Public Health Service. Chlorides decreased after 1970 and were down to 85 mg/l in 1972, perhaps assisted by abnormally high rainfall that year. The deicing ban was lifted in December 1972.

Figure 17 illustrates another change of groundwater quality with time. Here seasonal variations in nitrate measured in groundwater near a sewage treatment plant in Fresno, California, are plotted. A significant annual cycle is apparent with a maximum in the fall and a minimum in the spring. This fluctuation can be attributed to the discharge of high nitrogen content wastes from wineries in the area during the fall of each year. It is clear that frequent sampling is necessary to define these short-term changes.

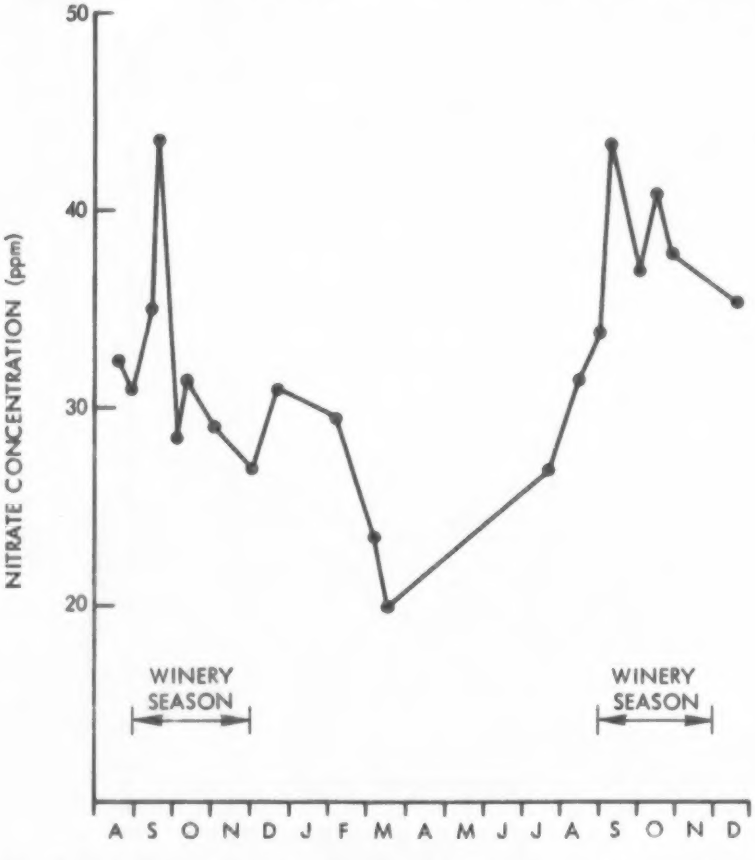


Figure 17. Seasonal variation in nitrate concentration for groundwater at Fresno, California (Schmidt, 1972).

EXAMPLE 4 — QUALITY VARIATION WITH DISTANCE. Figure 18 presents the variation in electrical conductivity of groundwater along the length of the Santa Ana River Basin in California. Electrical conductivity (EC) is an inexpensive measure of total dissolved solids; normally TDS is about 60 percent of EC. The pronounced increase in conductivity in a downstream direction can be attributed to a combination of urbanization, wastewater disposal, and artificial recharge of poorer quality imported water.

EXAMPLE 5 — QUALITY VARIATION WITH DEPTH. Figure 19 shows the variation of total dissolved solids with depth for groundwater in one portion of the Santa Clara-Calleguas area, Ventura County, California. At this location there are three distinct aquifers present. The samples from wells penetrating the aquifers indicate that there is little significant difference in quality in the two lower aquifers; however, the shallow perched water has been appreciably degraded, probably from waste disposal or seawater sources.

EXAMPLE 6 — AREA VARIATION IN QUALITY. Figure 20 is a map of total dissolved solids in groundwater of the Santa Clara-Calleguas area, Ventura County, California. Isosalinity lines cover the water-bearing portions of the area and are drawn on the basis of quality analyses from well water samples gathered throughout the basin.

EXAMPLE 7 — VERTICAL CROSS SECTION OF QUALITY. Figure 21 presents a vertical cross section of an alluvial aquifer in Michigan. Pollution resulted from disposal of industrial wastewaters into disposal ponds; chloride is used as an indicator of the pollution. Control of spread of the pollutant underground was accomplished by a combination of recharge ponds for cooling water and purge wells, both shown in Figure 21. These provided an effective hydraulic barrier to the spread of the pollution. Monitoring wells throughout the area enabled hydraulic and quality variations of the groundwater to be evaluated.

EXAMPLE 8 — MAPS OF POLLUTION PLUMES. Figure 22 outlines the plume of pollution in groundwater resulting from an oilfield brine disposal pit in southwestern Arkansas. This map shows that highly saline water, expressed by contours of chloride concentration, has spread generally southward in the direction of groundwater flow. The irregular shape of the pollution zone may be attributed to variations in permeability within the aquifer and to irregularities in the top surface of the shale which forms the bottom of the alluvial aquifer.

Figure 23 shows a long narrow plume of groundwater pollution produced by a landfill near Munich, West Germany. Some 70 monitoring wells were measured biweekly at this site for chloride, electrical conductivity, and temperature. Only chloride concentrations are shown in Figure 23; however, all three indicators of pollution display nearly identical configurations, suggesting that they are conservative and hence useful parameters for detection of subsurface pollution.

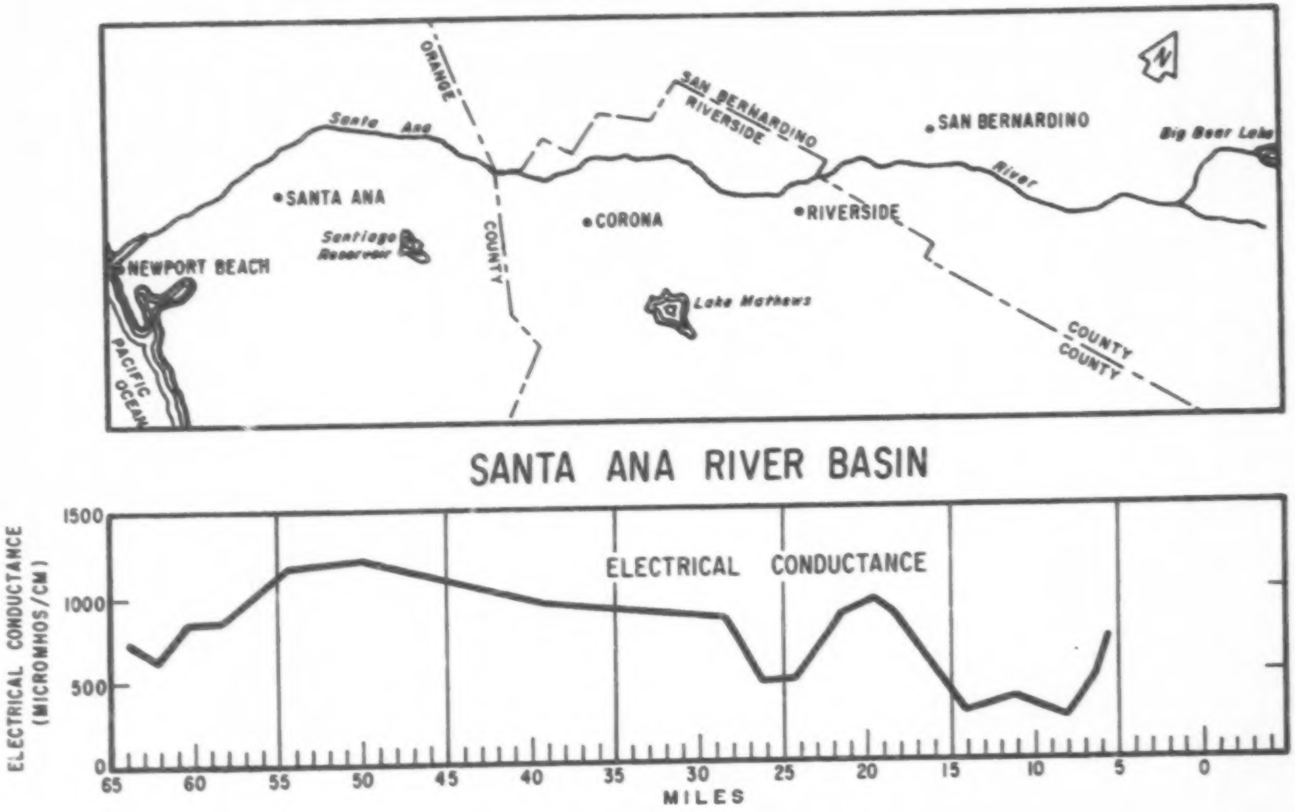


Figure 18. Variation in electrical conductivity of groundwater along the length of the Santa Ana River Basin, California (California Department of Water Resources, December 1974).

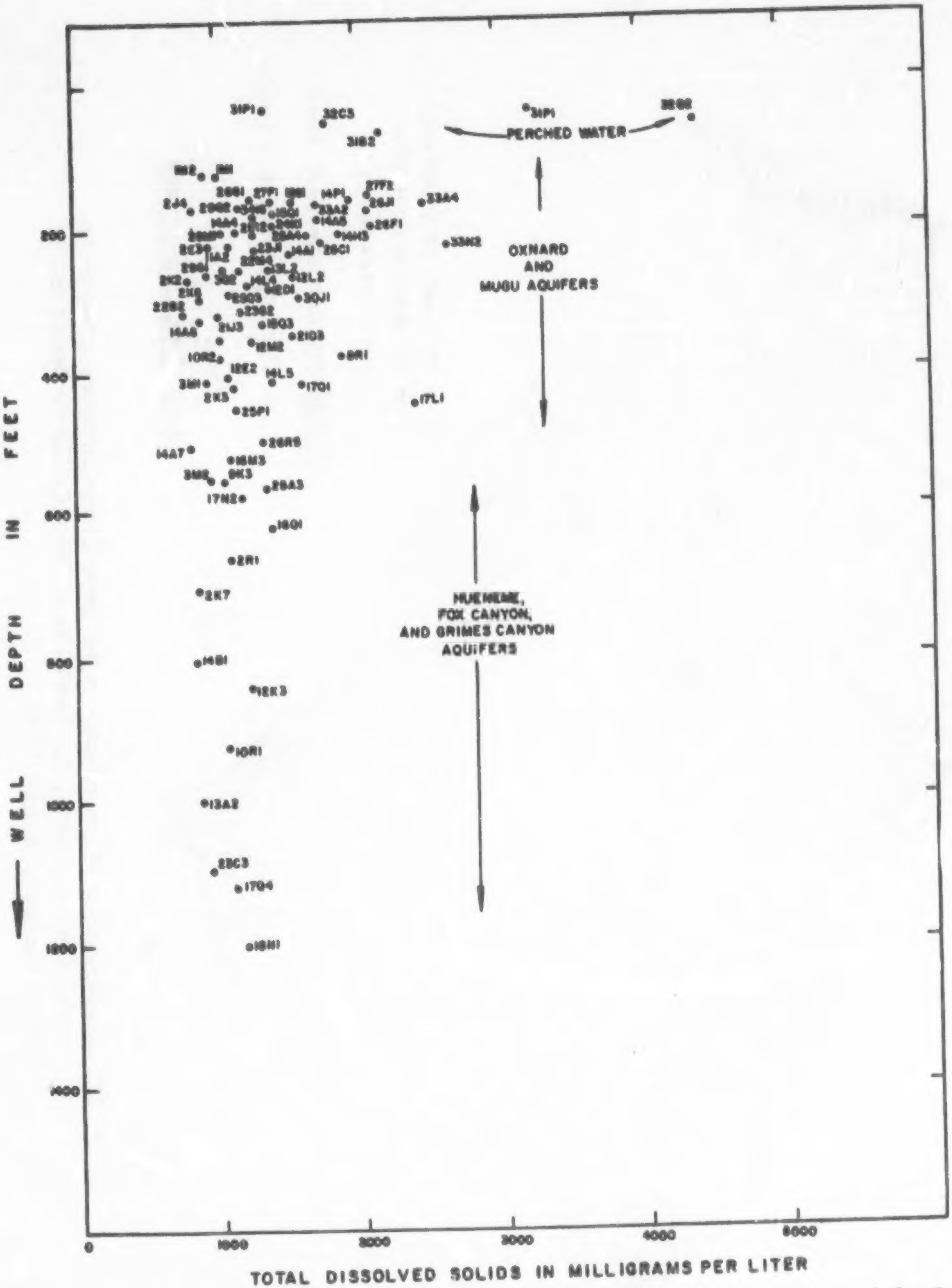


Figure 19. Variation of total dissolved solids with well depth in a portion of the Santa Clara-Calleguas groundwater basin, Ventura County, California (California Department of Water Resources, August 1974).

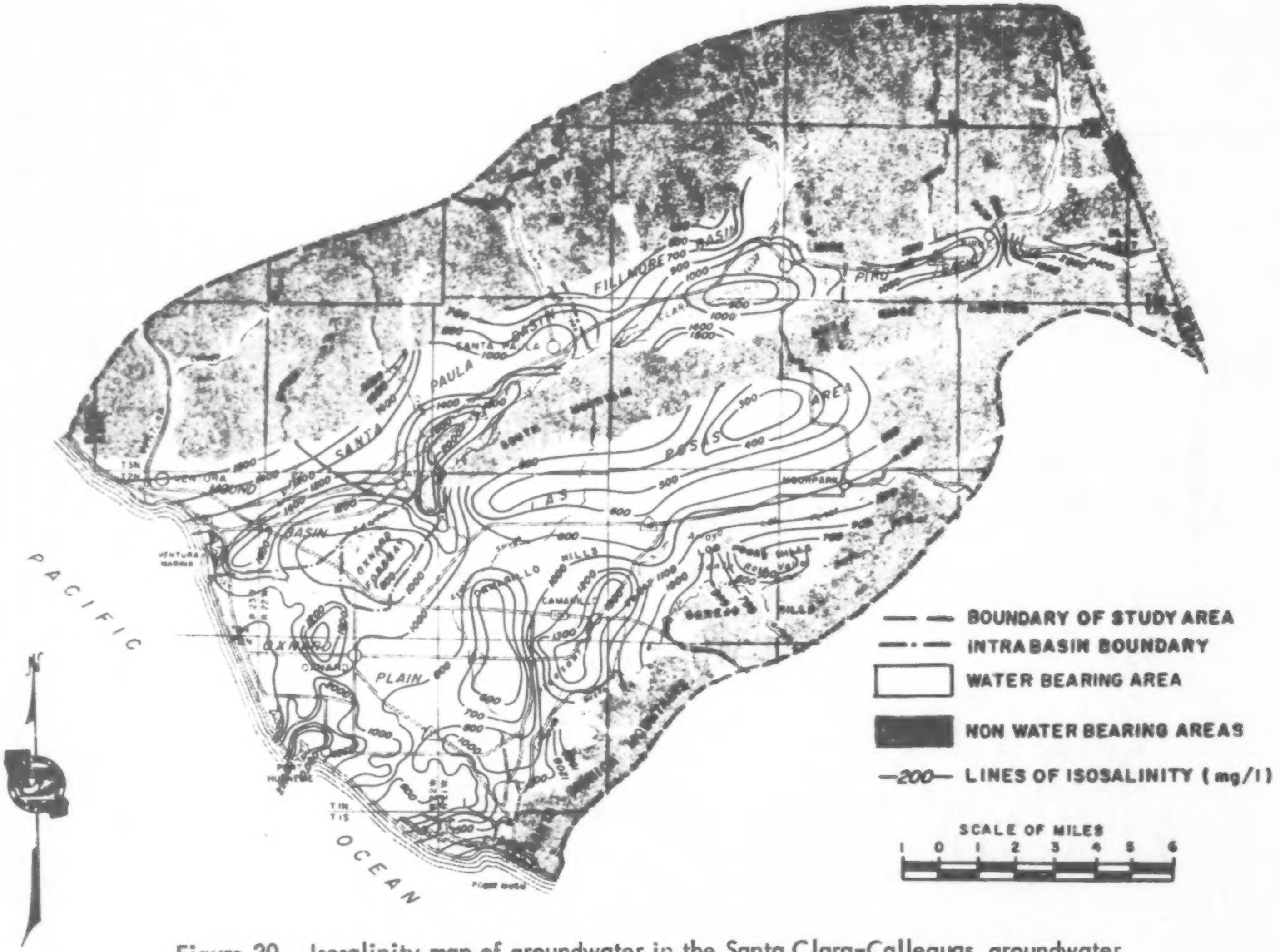

BOUNDARY OF STUDY AREA
INTRABASIN BOUNDARY
WATER BEARING AREA
NON WATER BEARING AREAS
—200— LINES OF ISOSALINITY (mg/l)
SCALE OF MILES
1 0 1 2 3 4 5 6
PACIFIC
OCEAN
N
FILLMORE
BASIN
PIRU
SANTA
PAULA
BASIN
LAS
POSAS
AREA
MOUND
BASIN
OXNARD
PLAIN
CAMARILLO
HILLS
VENTURA
SANTA PAULA
MOORPARK
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1800
2000

Figure 20. Isosalinity map of groundwater in the Santa Clara-Calleguas groundwater basin, Ventura County, California, as of 1966 (California Department of Water Resources, August 1974).

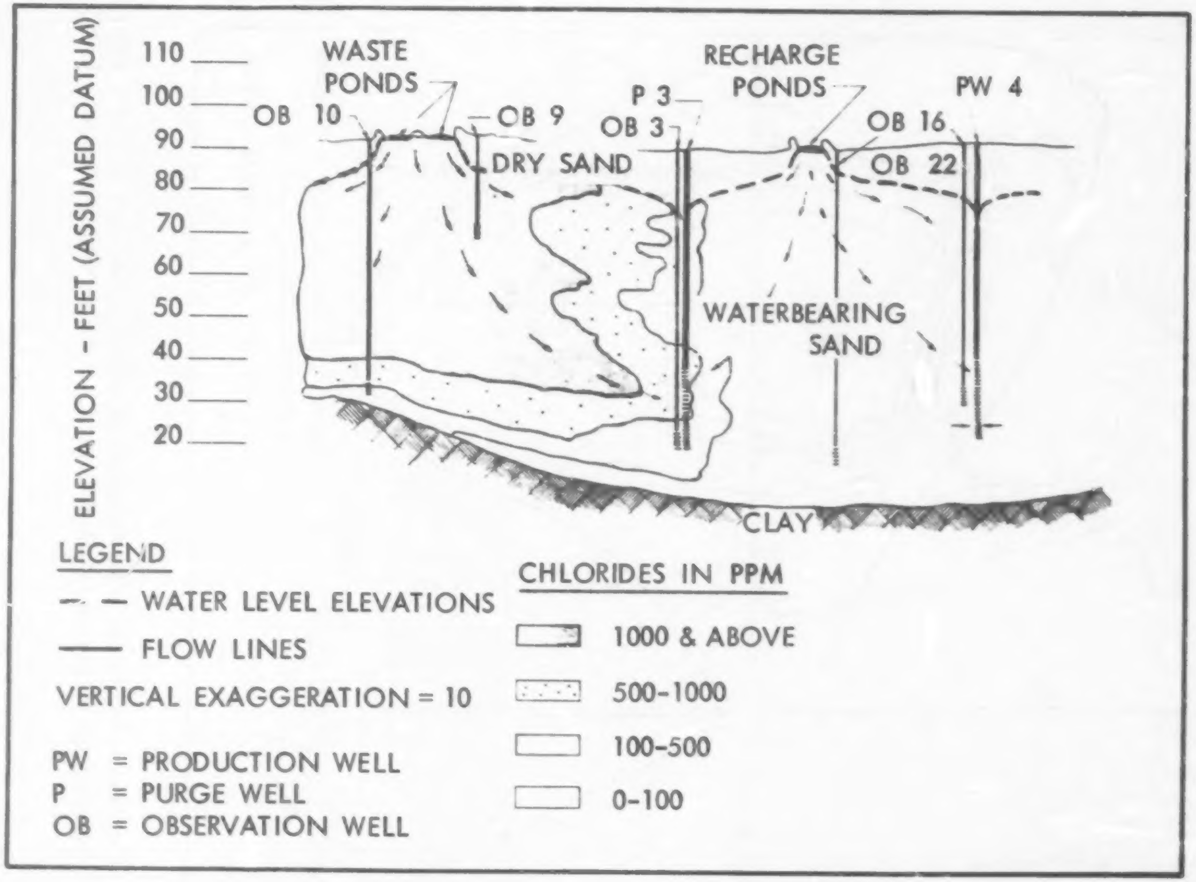

ELEVATION - FEET (ASSUMED DATUM)
110
100
90
80
70
60
50
40
30
20
WASTE PONDS
OB 10
OB 9
DRY SAND
P 3
OB 3
RECHARGE PONDS
OB 16
OB 22
PW 4
WATERBEARING SAND
CLAY
LEGEND
WATER LEVEL ELEVATIONS
FLOW LINES
VERTICAL EXAGGERATION = 10
PW = PRODUCTION WELL
P = PURGE WELL
OB = OBSERVATION WELL
CHLORIDES IN PPM
1000 & ABOVE
500-1000
100-500
0-100

Figure 21. Vertical cross section showing groundwater pollution movement from waste disposal ponds and control by cooling water recharge ponds and purge wells (Burt, 1972).

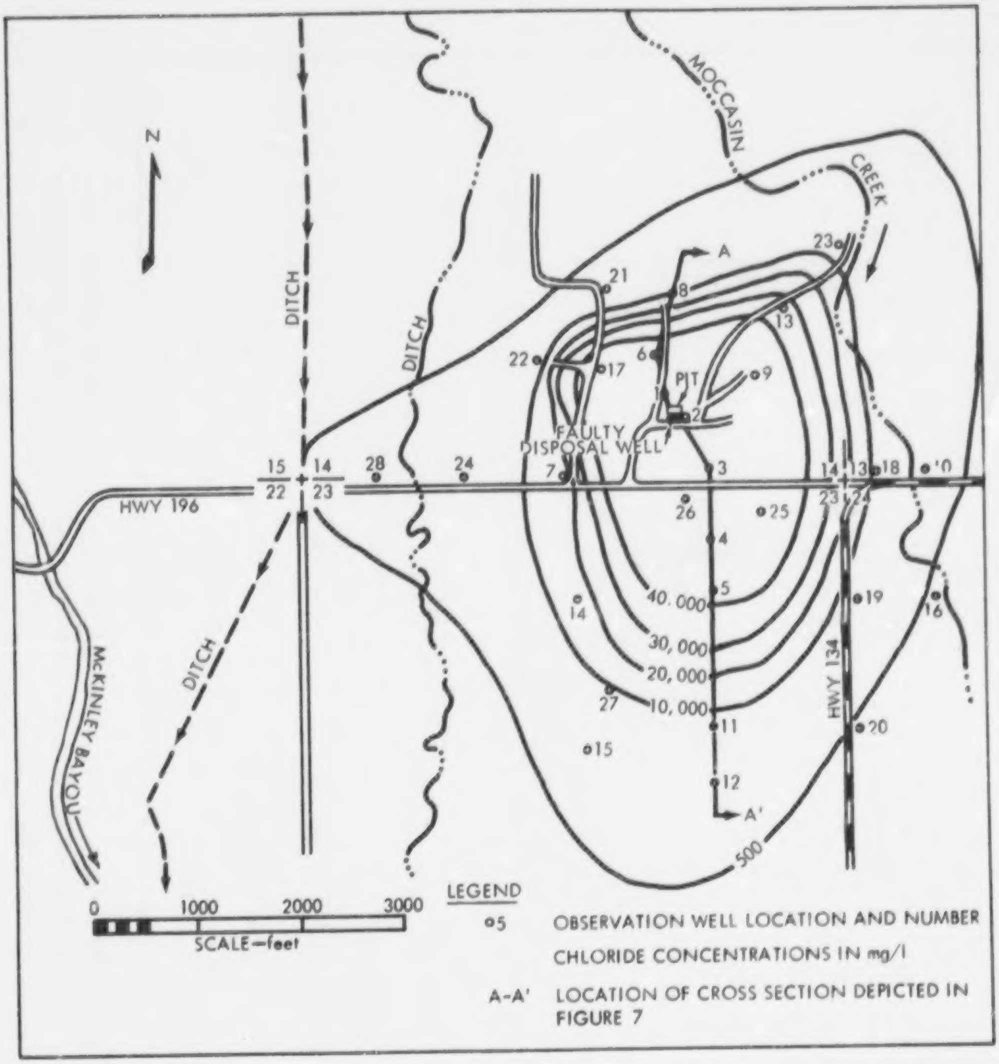

N
DITCH
DITCH
DITCH
MOCCASIN
CREEK
A
A'
PIT
FAULTY DISPOSAL WELL
15
14
22
23
14
13
23
24
HWY 196
HWY 134
McKINLEY BAYOU
21
8
23
13
22
17
6
9
1
2
7
3
28
24
26
25
18
10
4
5
14
19
16
27
11
15
12
20
40,000
30,000
20,000
10,000
500
0
1000
2000
3000
SCALE—feet
LEGEND
○5 OBSERVATION WELL LOCATION AND NUMBER
CHLORIDE CONCENTRATIONS IN mg/l
A-A' LOCATION OF CROSS SECTION DEPICTED IN FIGURE 7

Figure 22. Contours of chloride concentration in groundwater surrounding a brine disposal pit in southwestern Arkansas (modified after Fryberger, 1975).

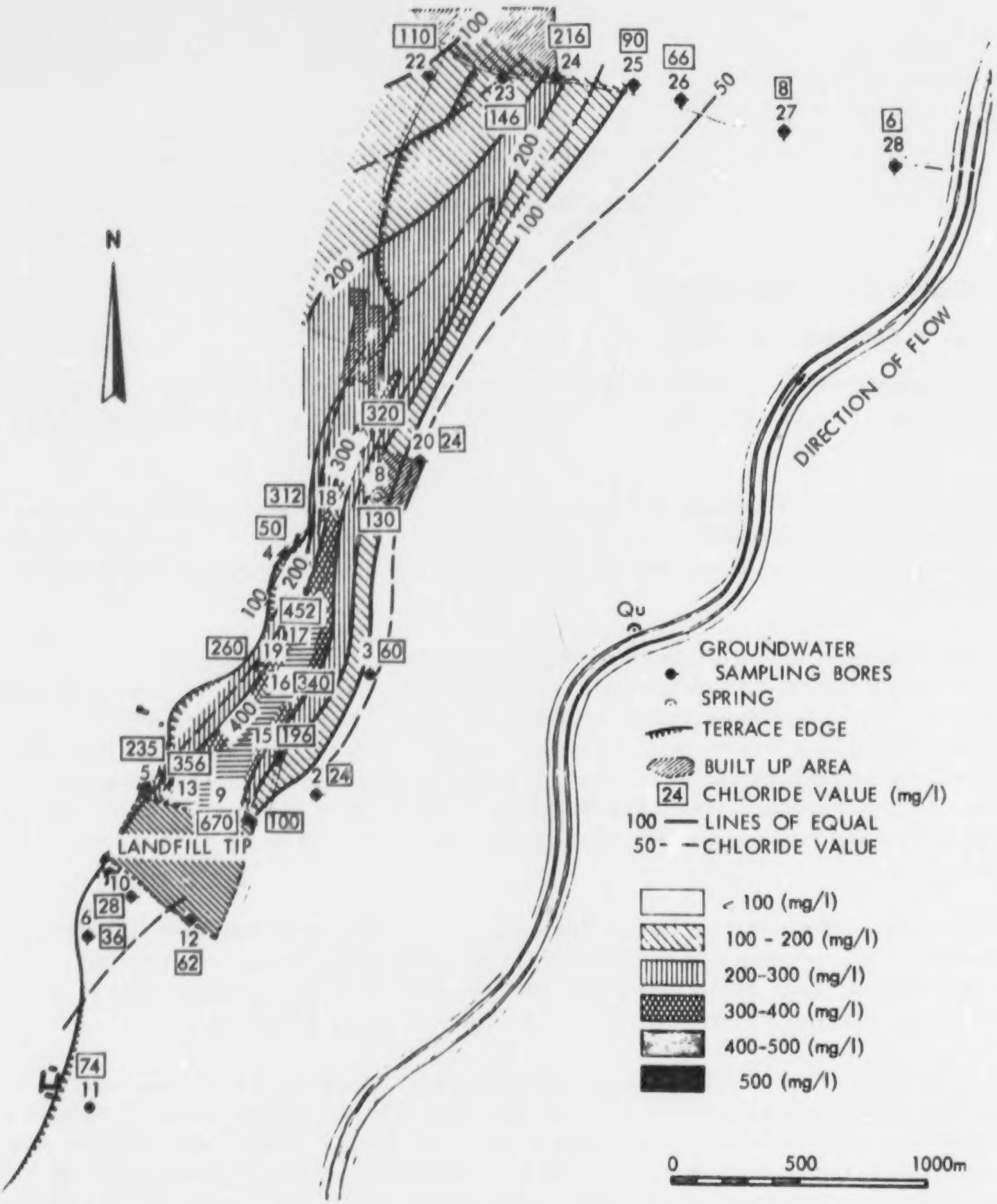

N
110
22
216
24
23
146
90
25
66
26
8
27
6
28
100
200
50
DIRECTION OF FLOW
320
20
24
312
18
8
130
50
4
300
452
17
260
19
3
60
16
340
400
15
196
235
5
356
13
9
2
24
670
100
LANDFILL TIP
10
28
6
36
12
62
74
11
Qu
GROUNDWATER SAMPLING BORES
SPRING
TERRACE EDGE
BUILT UP AREA
24 CHLORIDE VALUE (mg/l)
100 — LINES OF EQUAL
50- - CHLORIDE VALUE
< 100 (mg/l)
100 - 200 (mg/l)
200-300 (mg/l)
300-400 (mg/l)
400-500 (mg/l)
500 (mg/l)
0
500
1000m

Figure 23. Plume of groundwater pollution from a landfill near Munich, West Germany, shown by lines of chloride concentration (Cole, 1975).

SECTION III

GROUNDWATER QUALITY

HYDROGEOLOGIC FRAMEWORK

Geologic Formations as Aquifers

Permeable rock formations which store and transmit significant quantities of water are known as aquifers. A variety of geologic formations can act as aquifers.

The most widely developed aquifers in the United States consist of unconsolidated alluvial deposits, chiefly gravels and sands. These geologic features occur as water courses, buried valleys, plains, or intermontane valleys.

Limestone, a consolidated sedimentary rock, serves as an important aquifer when sizable proportions of the original rock have been dissolved and removed. Openings may range from microscopic pores to large solution caverns forming subterranean channels large enough to carry entire streams. Within large openings in limestone aquifers, groundwater can flow rapidly under turbulent conditions. Fractures and faults may allow limestones to serve as significant aquifers. Springs are frequently found in limestone areas.

Volcanic rocks such as basalt flows can form highly permeable aquifers. Flow breccias, porous zones between lava beds, lava tubes, shrinkage cracks, faults, and joints are other permeable zones in volcanic rocks. Most of the largest springs in the United States originate in basalt.

Sandstones and conglomerates represent cemented forms of sand and gravels. Sandstones function best as aquifers where they are only partially cemented or where joints, fractures, or faults are present. Crystalline and metamorphic rocks are usually relatively impermeable; however, groundwater may be developed by shallow wells under fractured or weathered conditions.

The following underground situations include most field conditions. The differences among them are important to waste disposal practices and to management of pollution problems.

- Unconsolidated granular materials extending downward from the ground surface to great depths: Beneath the ground surface in many places are loose granular materials, chiefly clays, silts, and sands, which may represent soil near the ground surface and sedimentary material below. Water and dissolved waste materials move en masse through pores surrounding the mineral particles.
- Unconsolidated granular materials at the ground surface underlain at shallow depths by dense rocks with linear openings: In many places the soils, loose sedimentary materials, or residual weathered materials are only a few feet or a few tens-of-feet thick and are underlain by dense rocks, the only openings in which are joints or solution channels. Water and waste materials move through both types of media.
- Dense rocks at the ground surface: The only movement is through interconnecting joints or solution channels.

The permeability of underground strata may vary by several orders of magnitude, and large variations can often be found over short distances. Some generalizations regarding permeability follow:

- In the vertical direction, the contrast in permeability between loose granular soil and underlying jointed rock can be very large.
- Zones of uniform permeability tend to be associated with particular rock strata.
- Where interbedded sedimentary rocks are flat or gently inclined, the changes of permeability in the vertical direction are frequent and large.
- Changes of permeability in the horizontal direction, although common, are in many cases more gradual than in the vertical direction.

An unconfined aquifer is one where a water table forms the upper surface of the zone of saturation (see the upper aquifer in Figure 24). A water table is a surface representing the level of atmospheric pressure within an aquifer. Fluctuations in the water table correspond to changes in the volume of water in storage within an aquifer.

A confined (or artesian) aquifer is one where groundwater is confined, under pressure greater than atmospheric, by overlying less permeable strata. If a well penetrates a confined aquifer, the water level will rise above the bottom of the confining bed, as shown in Figure 24. Variations of water levels in wells penetrating confined aquifers result from pressure

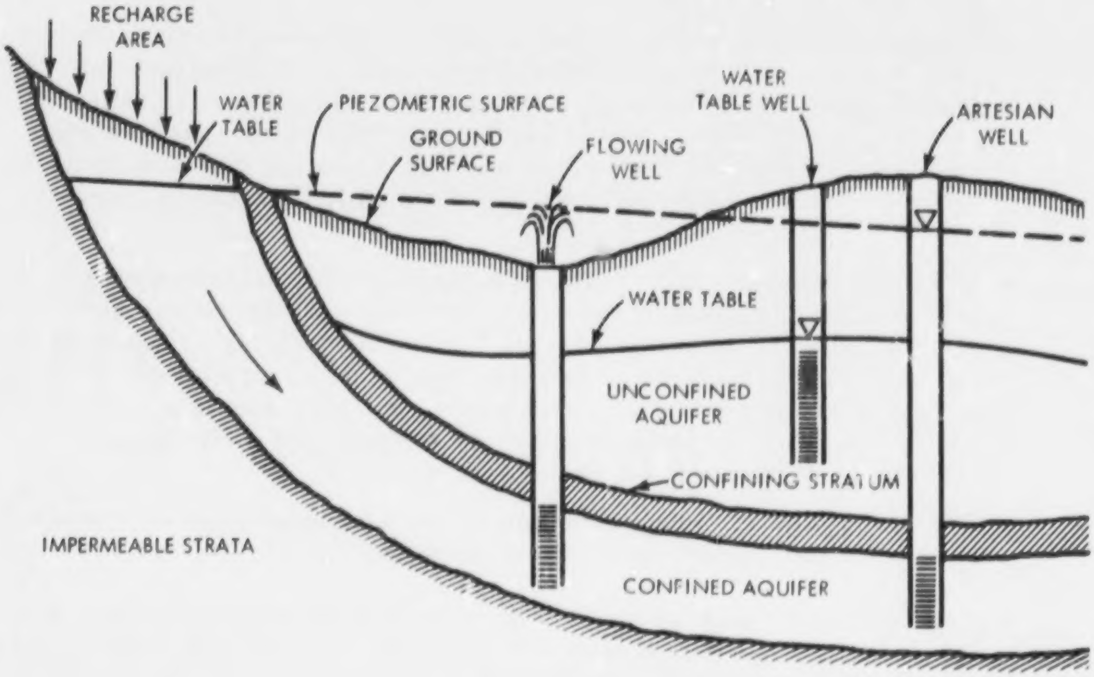

RECHARGE AREA
WATER TABLE
PIEZOMETRIC SURFACE
GROUND SURFACE
FLOWING WELL
WATER TABLE WELL
ARTESIAN WELL
WATER TABLE
UNCONFINED AQUIFER
CONFINING STRATUM
IMPERMEABLE STRATA
CONFINED AQUIFER

Figure 24. Unconfined and confined aquifers (Todd, 1959).

changes within the aquifer. The piezometric surface of a confined aquifer (see Figure 24) is an imaginary surface defining the hydrostatic pressure of the water in the aquifer.

Groundwater Movement

Most groundwater moves in accordance with Darcy's Law, which states that the velocity is directly proportional to the permeability of the aquifer and the hydraulic gradient. Typical groundwater flow velocities fall in the range of 5 feet per year to 5 feet per day; however, exceptionally higher velocities have been measured in highly permeable outwash glacial deposits, in fractured basalts and granitic rocks, and in cavernous limestones.

Essentially all groundwater is in motion from its source of recharge to its point of discharge. Natural recharge occurs from precipitation and surface water bodies; artificial recharge results from acts of man, such as by irrigation. Groundwater discharges naturally to springs, surface water bodies, and the ocean. Wells and drains function as manmade discharge points for groundwater.

Pollutants tend to move in the direction of flow of the surrounding groundwater. Within confined aquifers water movement is roughly horizontal because of the negligible vertical movement within the confining strata. There may be in certain situations, however, large vertical head gradients which induce vertical flows from one strata to another. In unconfined aquifers the groundwater also flows generally horizontally beneath a gently sloping water table. In the unsaturated zone above a water table, water usually percolates vertically downward to the water table. Less permeable layers may cause saturated conditions (perched groundwater) and allow horizontal movement.

Water in the saturated zone (below the water table) tends to move faster at relatively shallow depths than that at great depths. Where groundwater occurs to great depths, it is reasonable to consider an upper zone of rapid circulation, a middle zone of delayed circulation, and the lowest zone of very slow water circulation.

Natural Chemical Quality

All groundwater contains natural chemical constituents in solution. The kinds and amounts of constituents depend upon the geochemical environment, movement, and source of the groundwater. Typically, concentrations of dissolved constituents in groundwater exceed those in surface water. Also, salinities tend to be higher in arid regions and where drainage is poor.

Chemical constituents originate primarily from solution of rock materials. The geologic history of groundwater governs its salinity. Common chemical constituents of groundwater include:

Cations	Anions	Undissociated
Calcium	Carbonate	Silica
Magnesium	Bicarbonate	
Sodium	Sulfate	
Potassium	Chloride	
	Nitrate	

An abundance classification of dissolved solids in fresh water is shown in Table 6. Frequency distributions of various constituents are shown in Figure 25.

Table 7 provides a convenient summary of the major natural chemical constituents in groundwater in terms of their sources and their effects upon the usability of water.

The chemical quality of groundwater is often conveniently described for domestic and industrial use in terms of its salinity and its hardness. Salinity refers to the concentration of total dissolved solids present in the water. Hardness is a measure of the calcium and magnesium content and is usually expressed as the equivalent of calcium carbonate. Table 8 lists classifications of water by salinity and hardness.

TABLE 6. RELATIVE ABUNDANCE OF DISSOLVED SOLIDS IN POTABLE WATER (Davis and DeWiest, 1966)

Major Constituents (1.0 to 1000 ppm)	Secondary Constituents (0.01 to 10.0 ppm)	Minor Constituents (0.0001 to 0.1 ppm)	Trace Constituents (generally less than 0,001 ppm)
Sodium	Iron	*Antimony	Beryllium
Calcium	Strontium	Aluminum	Bismuth
Magnesium	Potassium	Arsenic	*Cerium
Bicarbonate	Carbonate	Barium	Cesium
Sulfate	Nitrate	Bromide	Gallium
Chloride	Fluoride	*Cadmium	Gold
Silica	Boron	*Chromium	Indium
		Cobalt	Lanthanum
		Copper	*Niobium
		*Germanium	Platinum
		Iodide	Radium
		Lead	*Ruthenium
		Lithium	*Scandium
		Manganese	Silver
		Molybdenum	*Thallium
		Nickel	*Thorium
		Phosphate	Tin
		*Rubidium	*Tungsten
		Selenium	Ytterbium
		*Titanium	*Yttrium
		Uranium	*Zirconium
		Vanadium	
		Zinc	

---

*These elements occupy an uncertain position in the list.

Besides solution of rock materials, other natural sources of salinity in groundwater include:

- Water of volcanic origins
- Evapotranspiration through native vegetation
- Airborne salts.

Within a large body of groundwater the natural chemical composition of the water tends to be relatively consistent, although the concentration of minerals in solution may be variable. However, where geologic differences or multiple sources exist, significant salinity differences occur. Time variations of groundwater quality under natural conditions are minor in comparison with surface water quality changes.

Groundwater under natural conditions tends to increase in salinity with depth. Most of the geologic formations containing groundwater in the United States are underlain by waters varying from brackish to highly saline. Density and permeability differences act to maintain a separation between these waters and the overlying fresh groundwater.

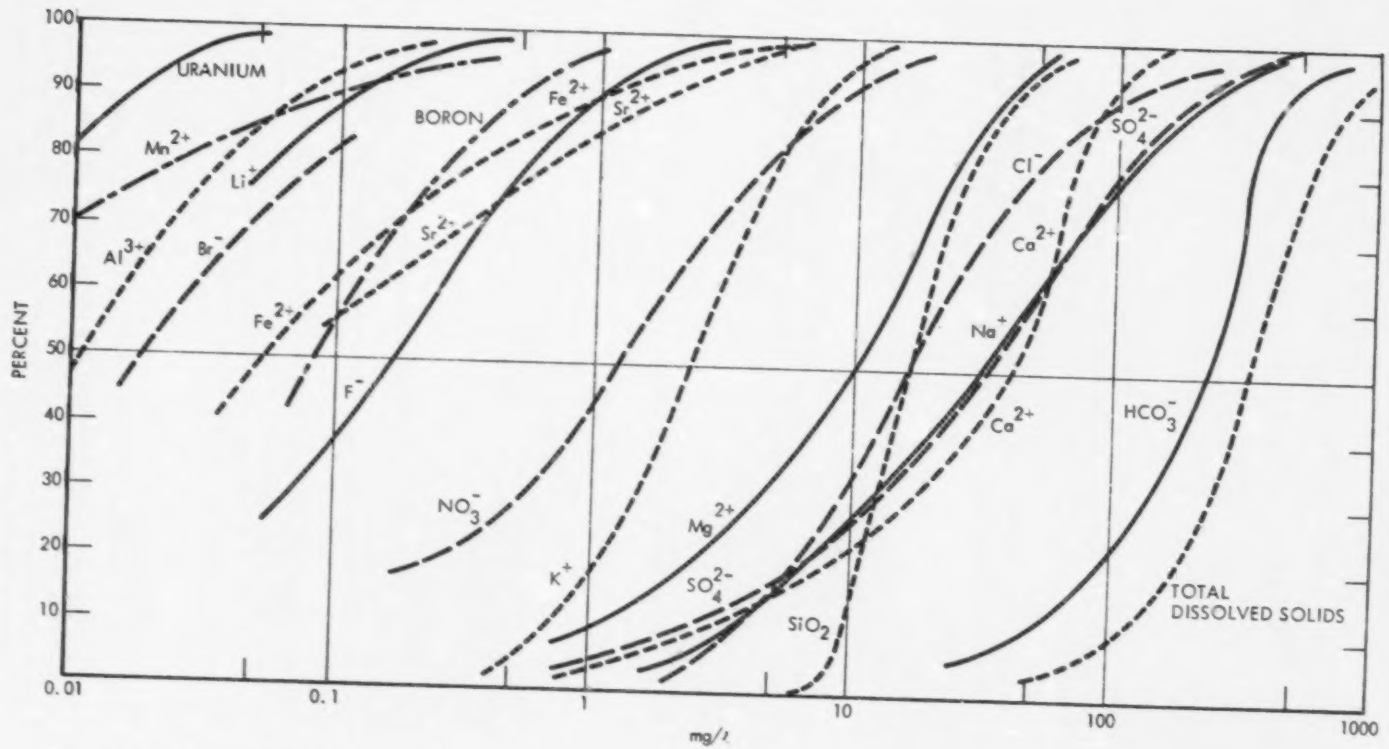


Figure 25. Cumulative curves showing the frequency distribution of various constituents in potable water (modified after Davis and DeWiest, 1966).

TABLE 7. MAJOR NATURAL CONSTITUENTS IN GROUNDWATER — THEIR SOURCES AND EFFECTS UPON USABILITY (modified after Miller et al., 1974)

Silica (SiO_2)

Sources: Feldspars, ferromagnesium and clay minerals, amorphous silica, chert, opal.

Effect: In the presence of calcium and magnesium, silica forms a scale in boilers and on steam turbines that retards heat; the scale is difficult to remove. Silica may be added to soft water to inhibit corrosion of iron pipes.

Iron (Fe)

Sources (natural): Igneous Rocks — amphiboles, ferromagnesian micas, ferrous sulfide (FeS), ferric sulfide or iron pyrite (FeS_2), magnetite (Fe_3O_4) — and Sandstone Rocks — oxides, carbonates, and sulfides or iron clay minerals.

Effect: More than 0.1 ppm precipitates after exposure to air; causes turbidity, stains plumbing fixtures and laundry and cooking utensils, and imparts objectionable tastes and colors to foods and drinks. More than 0.2 ppm is objectionable for most industrial uses.

Manganese (Mn)

Sources: Manganese in natural water probably comes most often from soils and sediments. Metamorphic and sedimentary rocks and mica biotite and amphibole hornblende minerals contain large amounts of managanese.

Effect: More than 0.2 ppm precipitates upon oxidation; causes undesirable tastes, deposits on foods during cooking, stains plumbing fixtures and laundry, and fosters growths in reservoirs, filters, and distribution systems. Most industrial users object to water containing more than 0.2 ppm.

Calcium (Ca) and Magnesium (Mg)

Sources: Calcium — Amphiboles, feldspars, gypsum, pyroxenes, aragonite, calcite, dolomite, clay minerals.
Magnesium — Amphiboles, olivine, pyroxenes, dolomite, magnesite, clay minerals.

Effect: Calcium and magnesium combine with bicarbonate, carbonate, sulfate, and silica to form heat retarding, pipe-clogging scale in boilers and in other heat-exchange equipment. Calcium and magnesium combine with ions of fatty acid in soaps to form soapsuds. A high concentration of magnesium has a laxative effect, especially on new users of the supply.

Sodium (Na) and Potassium (K)

Sources: Sodium — Feldspars (albite); clay minerals; evaporites, such as halite (NaCl) and mirabilite ($Na_2SO_4 \cdot 10H_2O$).
Potassium — Feldspars (orthoclase and microcline), feldspathoids, some micas, clay minerals.

Effect: More than 50 ppm sodium and potassium in the presence of suspended matter causes foaming, which accelerates scale formation and corrosion in boilers. Sodium and potassium carbonate in recirculating cooling water can cause deterioration of wood in cooling towers. More than 65 ppm of sodium can cause problems in ice manufacture.

Carbonate (CO_3) and Bicarbonate (HCO_3)

Sources: Bicarbonate — Biosphere; limestone; dolomite.

Effect: Upon heating, bicarbonate is changed into steam, carbon dioxide, and carbonate. The carbonate combines with alkaline earths — principally calcium and magnesium — to form a crustlike scale of calcium carbonate that retards flows of heat through pipe walls and restricts flow of fluids in pipes. Water containing large amounts of bicarbonate and alkalinity are undesirable in many industries.

(continued)

Table 7. (Continued)

Sulfate (SO_4)	
Sources:	Oxidation of sulfide ores; gypsum; anhydrite.
Effect:	Sulfate combines with calcium to form an adherent, heat-retarding scale. More than 250 ppm is objectionable in water in some industries. Water containing about 500 ppm of sulfate tastes bitter; water containing about 1,000 ppm may be cathartic.
Chloride (Cl)	
Sources:	Sedimentary rocks and evaporites; ocean tides force salty water upstream in tidal estuaries.
Effect:	Chloride in excess of 100 ppm imparts a salty taste, while concentrations of the order of 1000 or more may cause physiological damage. Food processing industries usually require less than 250 ppm. Some industries — textile processing, paper manufacturing, and synthetic rubber manufacturing — desire less than 100 ppm.
Fluoride (F)	
Sources:	Amphiboles (hornblende), apatite, fluorite, mica.
Effect:	Fluoride concentration between 0.6 and 1.7 ppm in drinking water has a beneficial effect on the structure and resistance to decay of children's teeth. Fluoride in excess of 1.5 ppm in some areas causes "mottled enamel" in children's teeth. Fluoride in excess of 6.0 ppm causes pronounced mottling and disfiguration of teeth.
Nitrate (NO_3)	
Sources:	Atmosphere; legumes, plant debris, and animal excrement.
Effect:	Water containing large amounts of nitrate (more than 100 ppm) is bitter tasting and may cause physiological distress. Water from shallow wells containing more than 45 ppm has been reported to cuase methemoglobinemia in infants. Small amounts of nitrate help reduce cracking of high-pressure boiler steel.
Dissolved Solids	
Sources:	The mineral constituents dissolved in water constitute the dissolved solids.
Effect:	More than 500 ppm is undesirable for drinking and many industrial uses. Less than 300 ppm is desirable for dyeing of textiles and the manufacture of plastics, pulp, paper, and rayon. Dissolved solids cause foaming in steam boilers; the maximum permissible content decreases with increases in operating pressure.

OCCURRENCE OF GROUNDWATER POLLUTION

Definition

Groundwater pollution is the degradation in the natural quality of groundwater produced by acts of man. Pollution may inhibit the use of the water or may create hazards to public health through toxicity or the spread of disease.

This definition follows that appearing in the Federal Water Pollution Control Act of 1972, and quoted in the Introduction to this report.

Distribution of Pollutants

If it were possible to see zones of groundwater pollution from an aerial vantage point, most would appear so small in relation to the total areas as to be termed scattered points of pollution. Areally extensive sources such

TABLE 8. CLASSIFICATIONS OF WATER
(Davis and DeWiest, 1966)

Based on Concentration of Total Dissolved Solids (TDS)	
Name	Concentration of TDS (parts per million)
Fresh	0-1,000
Brackish	1,000-10,000
Salty	10,000-100,000
Brine	More than 100,000
Based on Hardness	
Name	Hardness as $CaCO_3$ (parts per million)
Soft	0-60
Moderately Hard	61-120
Hard	121-180
Very Hard	More than 180

as irrigation return flows and seawater intrusion would be identified as nonpoint sources. A line source would result, for example, from recharge of sewage effluent in an ephemeral stream channel.

Figure 26 suggests by small dots on a map the distribution of groundwater pollution in a drainage basin. As indicated by the profile view at the top of Figure 26, most point sources of pollution will not penetrate through the zone of aeration; this is particularly true where the volume of pollutant is relatively small and where the water table is some distance below ground surface. The profile view of Site 5 in Figure 26 shows a pollutant that has reached the water table and has begun to migrate down-gradient with the groundwater flow.

Mechanisms of Pollution

Shallow aquifers are usually the most important sources of groundwater for water supply purposes, but the upper portions of these aquifers are also the most susceptible to pollution. The entry of pollutants to shallow aquifers occurs (1) directly through wells, (2) by downward percolation through the zone of aeration, (3) by induced recharge from surface water bodies, (4) by interaquifer flow, and (5) by upconing of deeper saline water due to overpumping of wells.

It should be recognized that the configuration of pollution entry into and movement within the underground is unique for each individual pollution

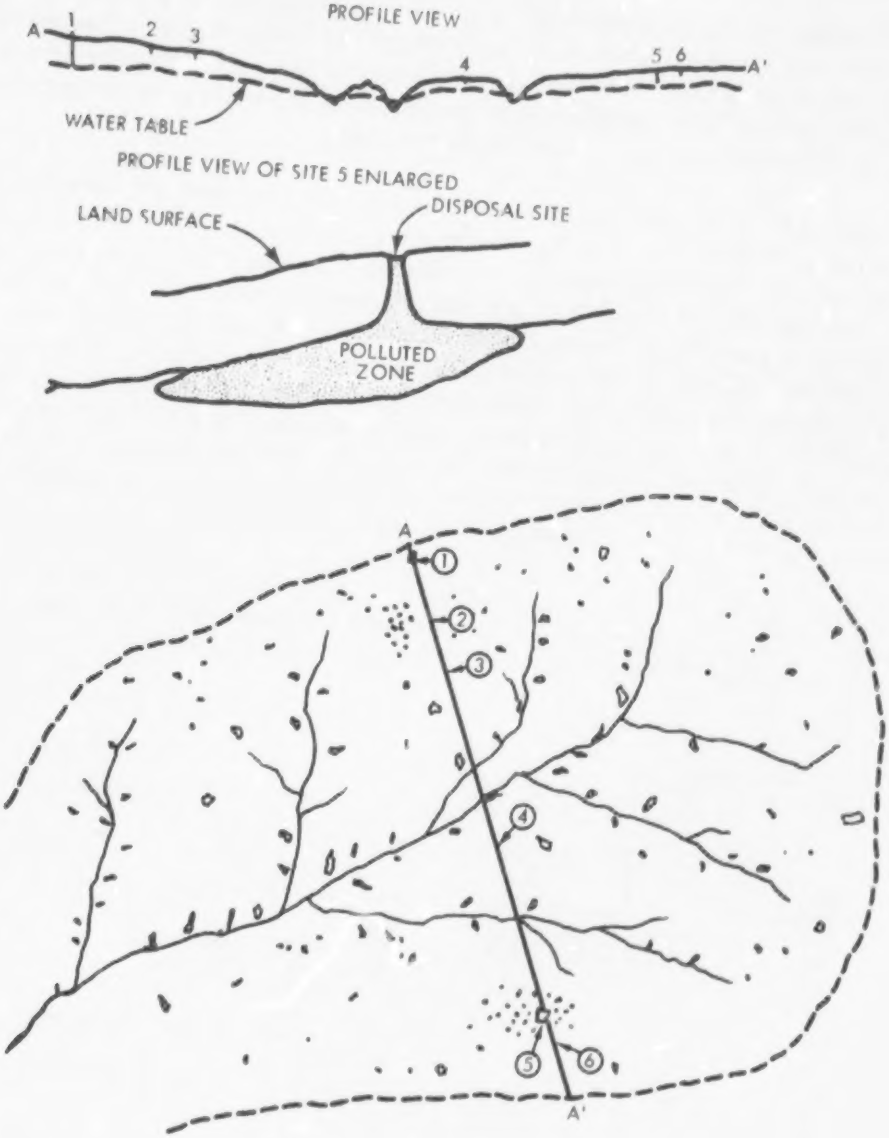

PROFILE VIEW
A
1
2
3
4
5 6
A'
WATER TABLE
PROFILE VIEW OF SITE 5 ENLARGED
LAND SURFACE
DISPOSAL SITE
POLLUTED ZONE
A
①
②
③
④
⑤
⑥
A'

Figure 26. A hypothetical drainage basin in a humid region showing in plan view the distribution of zones of polluted water in the upper part of the zone of saturation. Line AA' shows profile view across basin. At disposal sites 1 and 5 pollutants extend through zone of aeration and cause a polluted zone beneath the water table. Disposal sites 2, 3, 4, and 6 do not pollute the groundwater (modified after LeGrand, 1965b).

source. Furthermore, because there are many millions of groundwater pollution sources in the United States, it becomes apparent that the possibilities in terms of pollutant movement and distribution are virtually limitless. Notwithstanding this fact, typical flow patterns of groundwater pollutants for a variety of common situations can be described.

The diagrams on the following pages depict some of the frequently occurring pollution geometries. These emphasize vertical cross sections at pollution sources; horizontal pollution movement thereafter is discussed later. Whatever the particular source of pollution may be, these diagrams indicate the hydraulic relationships for a given situation. Where the local hydrogeology is known, paths of probable pollutant movement can be defined. With estimates of permeability, hydraulic gradient, and porosity available, rates of groundwater movement can be ascertained. Rates of pollutant movement are based on groundwater flow rates, chemical interactions with aquifer materials, and changes in water chemistry. Thus, pollutants travel at velocities equal to or less than that of the groundwater.

Figure 27 shows the local movement of effluent from a domestic septic tank system. The waste water flows vertically downward to the water table and then is distributed laterally within the groundwater body.

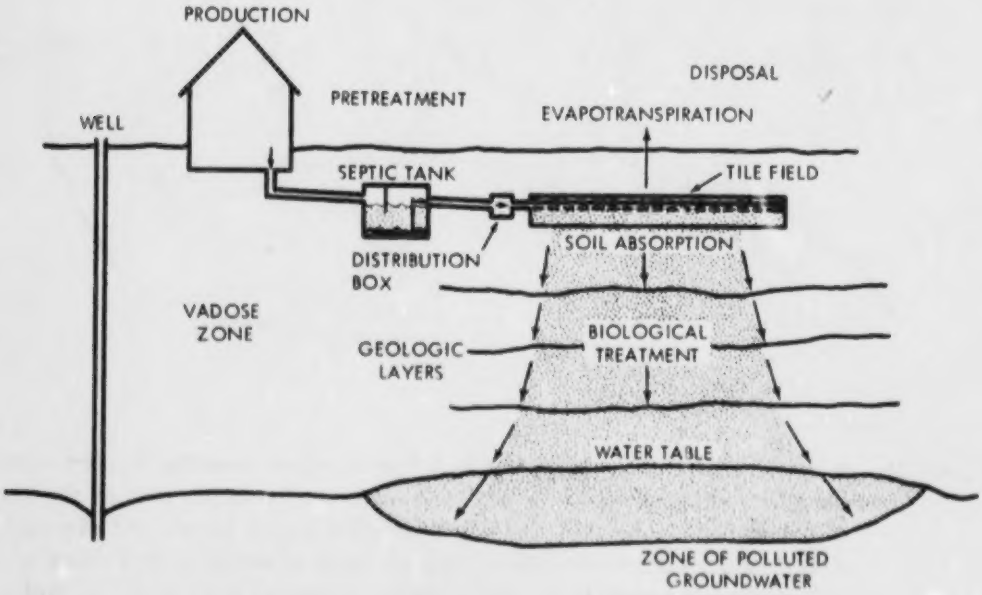

PRODUCTION
DISPOSAL
PRETREATMENT
WELL
EVAPOTRANSPIRATION
SEPTIC TANK
TILE FIELD
SOIL ABSORPTION
DISTRIBUTION BOX
VADOSE ZONE
GEOLOGIC LAYERS
BIOLOGICAL TREATMENT
WATER TABLE
ZONE OF POLLUTED GROUNDWATER

Figure 27. Disposal of household wastes through a conventional septic tank system (modified after Miller et al., 1974).

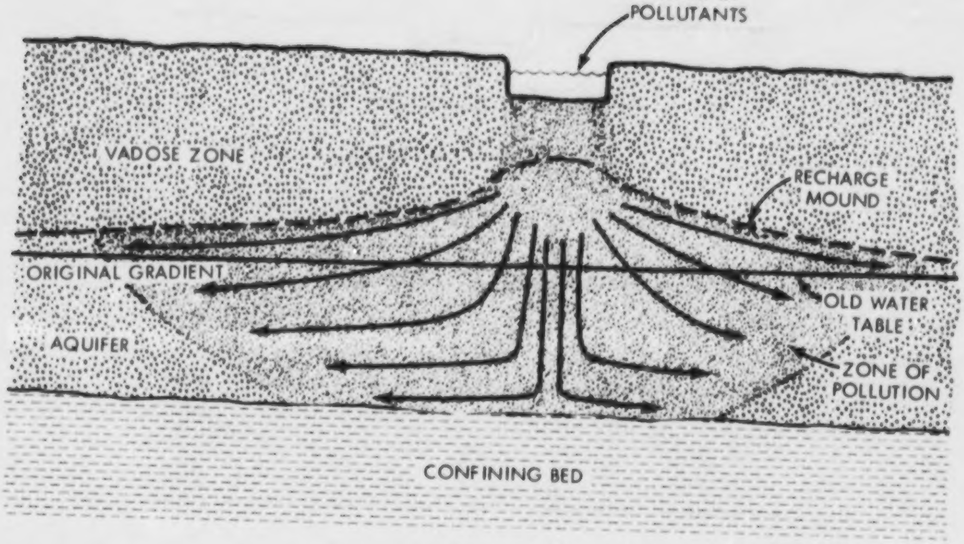


Figure 28. Diagram showing percolation of pollutants from a disposal pit to a water table aquifer (modified after Deutsch, 1963).

Figure 28 illustrates the flow of pollution from a surface source such as a disposal pit, lagoon, or basin. Note that the polluted water flows downward to form a recharge mound at the water table and then moves laterally outward below the water table. If significant layering exists above the water table, horizontal movement may occur in the vadose zone as suggested by Figure 29.

Figure 30 shows cross-sectional and plan views of groundwater pollution caused by a leaking sewer. The pollution drains downward to the water table and then flows laterally thereafter to form a line source of pollution beneath the sewer.

Figure 31 indicates how salt leached from a salt stockpile moves downward to the water table and thereafter laterally and vertically to a nearby pumping well. Figure 32 indicates pollution movement from a surface stream or lake to a nearby pumping well. The drawdown of the water table induces recharge of surface water to groundwater. Many municipal water supply wells are located adjacent to rivers in order to insure continuous water supplies. This is an important groundwater pollution mechanism where rivers are polluted. In arid areas where water tables are relatively deep, polluted surface water can percolate to groundwater regardless of pumping patterns.

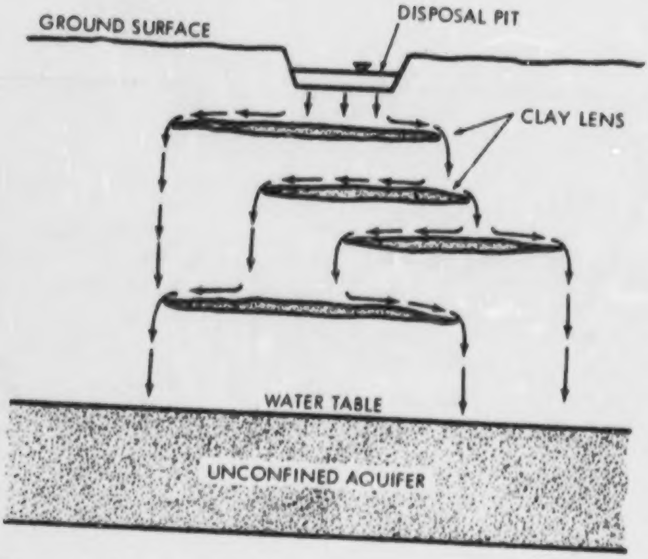

GROUND SURFACE
DISPOSAL PIT
CLAY LENS
WATER TABLE
UNCONFINED AQUIFER

Figure 29. Diagram showing the horizontal movement of pollutants beneath a disposal pit as a result of clay lenses in the vadose zone above the water table.

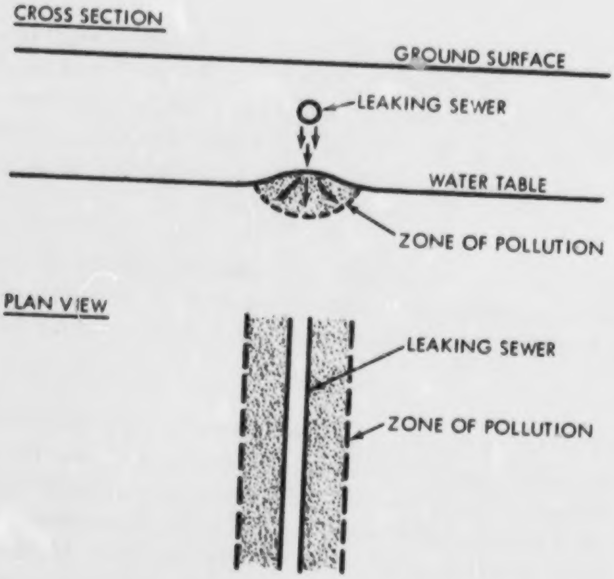

CROSS SECTION
GROUND SURFACE
LEAKING SEWER
WATER TABLE
ZONE OF POLLUTION
PLAN VIEW
LEAKING SEWER
ZONE OF POLLUTION

Figure 30. Illustration of a line source of groundwater pollution caused by a leaking sewer. The water table is situated below the sewer and is assumed to be horizontal.

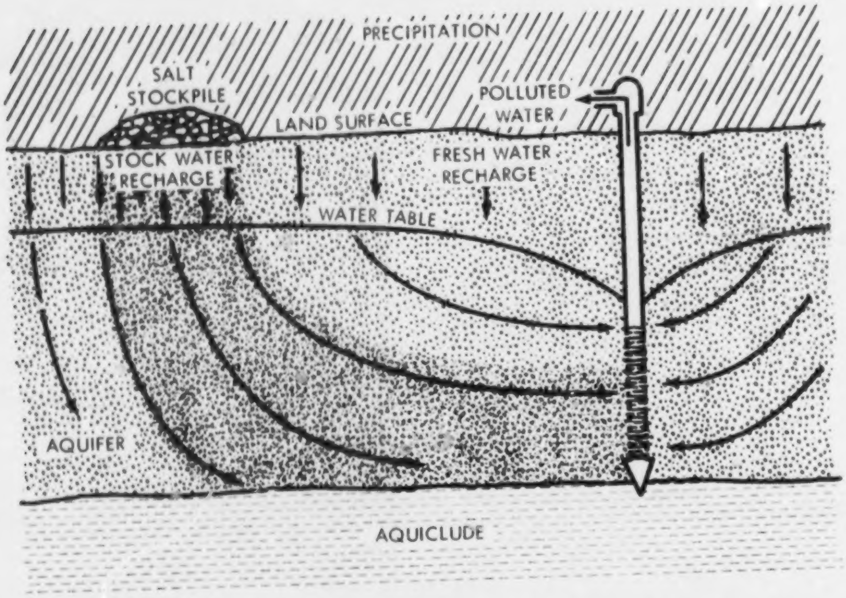

PRECIPITATION
SALT STOCKPILE
POLLUTED WATER
LAND SURFACE
STOCK WATER RECHARGE
FRESH WATER RECHARGE
WATER TABLE
AQUIFER
AQUICLUDE

Figure 31. Diagram showing pollution of an aquifer by leaching of surface solids (modified after Deutsch, 1963).

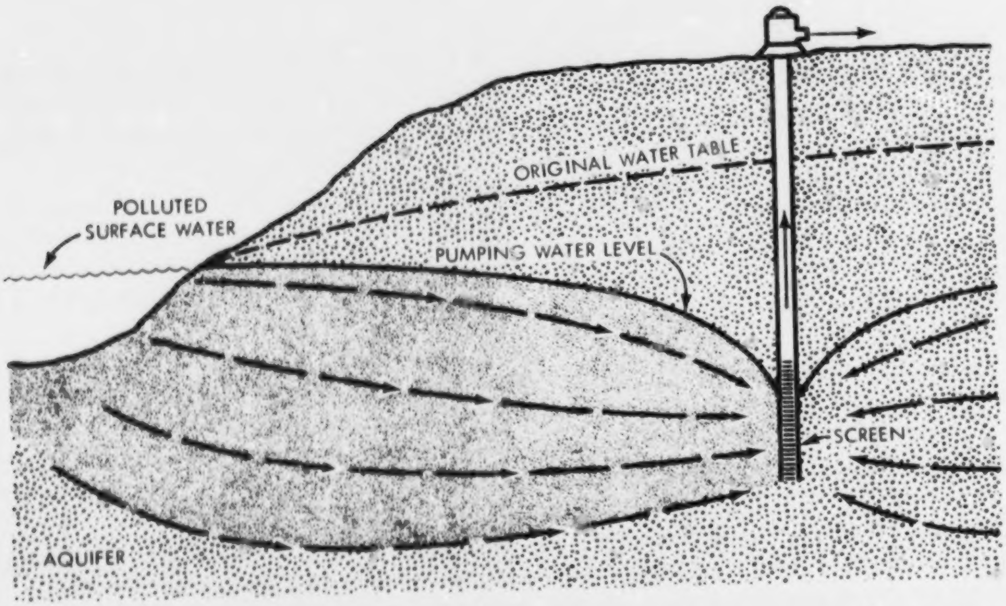

ORIGINAL WATER TABLE
POLLUTED SURFACE WATER
PUMPING WATER LEVEL
SCREEN
AQUIFER

Figure 32. Diagram showing how polluted water can be induced to flow from a surface stream to a well (modified after Deutsch, 1963).

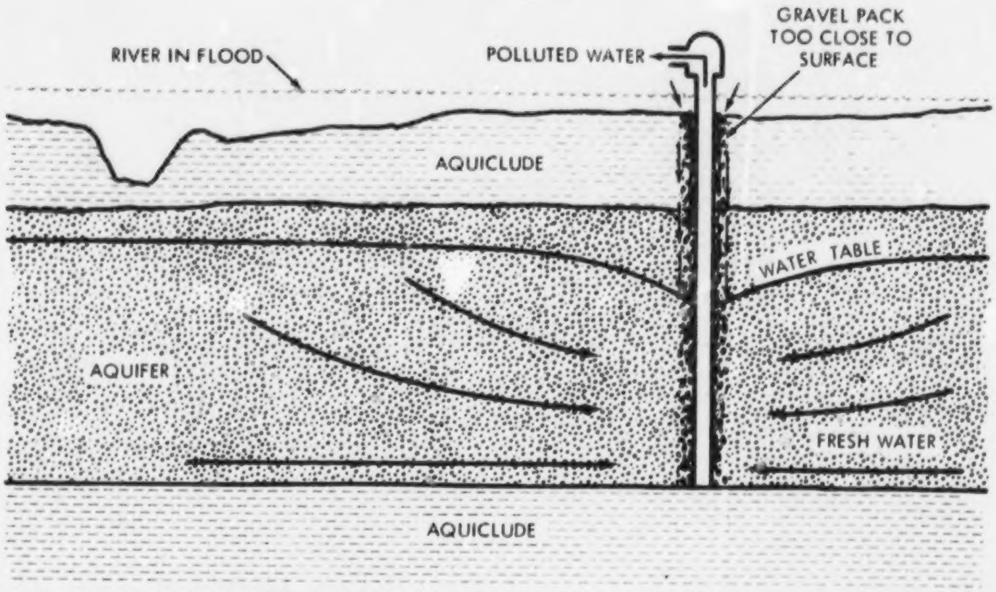


Figure 33. Diagram showing floodwater entering a well through an improperly sealed gravel pack (modified after Deutsch, 1963).

Figure 33 suggests how temporary flooding of a well can lead to groundwater pollution. Downward flow of polluted surface water occurs around the well casing if the well has been improperly sealed at the ground surface.

Figure 34 indicates how the disposal of pollutants into one well can be transported through the aquifer and lead to pollution of a nearby pumping well. Because a pumping well is a convergence point for groundwater over a large area, this collection mechanism increases the opportunity for obtaining polluted water from a pumping well.

Figure 35 outlines the flow patterns of pollutants entering a water table aquifer and a confined aquifer from an injection or recharge well. Note that the pollution tends to spread through the entire thickness of an aquifer and then move radially outward from the well.

Figure 36 illustrates the reversal of underground flows due to pumpage from one aquifer and hence the possibility to degrade the groundwater quality by interaquifer flow. Under natural conditions shown in the upper diagram, the water table of Aquifer A is higher than the piezometric surface of Aquifer B; therefore, groundwater tends to move downward through the

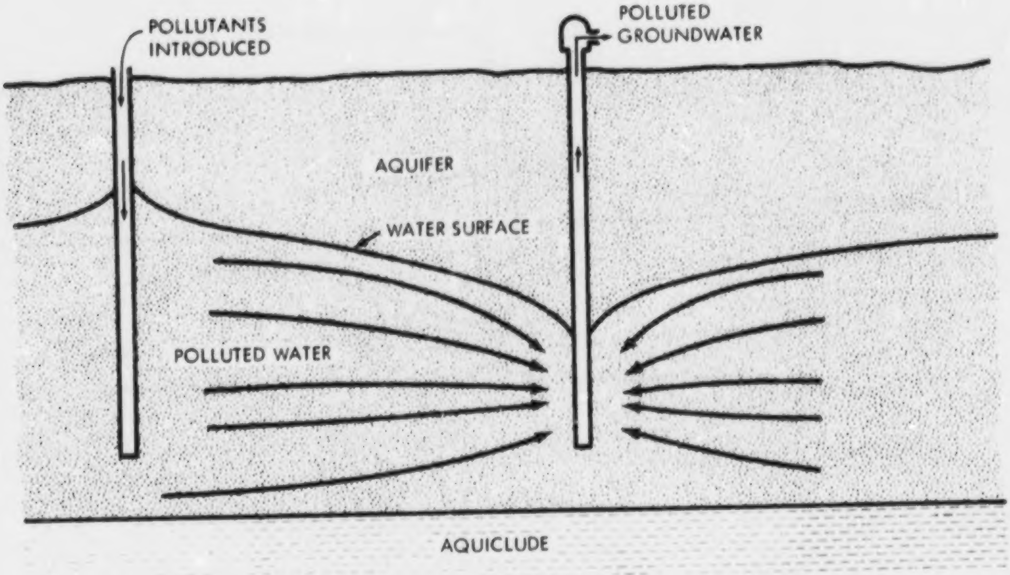


Figure 34. Diagram showing movement of pollutants from a recharge well to a nearby pumping well (modified after Deutsch, 1963).

semipermeable zone separating the two aquifers. In the lower diagram, however, pumping has interchanged the relative positions of the two water levels. As a result, the greater pressure in Aquifer B causes water to migrate upward into Aquifer A. If, as is often the case, the lower aquifer is more saline, this will cause the salt content of the upper aquifer to increase.

Figure 37 presents two situations of interaquifer flow through a nonpumping well penetrating more than one aquifer. In Figure 37(a) the water table stands above the piezometric surface so that water flows down the well into the deeper aquifer. But in Figure 37(b) the situation is reversed so that water rises through the well and invades the upper zone.

Figure 38 shows plan and profile views of a recharge pond overlying an unconfined aquifer with a sloping water table and with groundwater flowing from left to right. Under these conditions pollution from the pond extends a short distance upstream and is stabilized. The bulk of the pollutant moves away from the pond in a downgradient direction within clearly defined

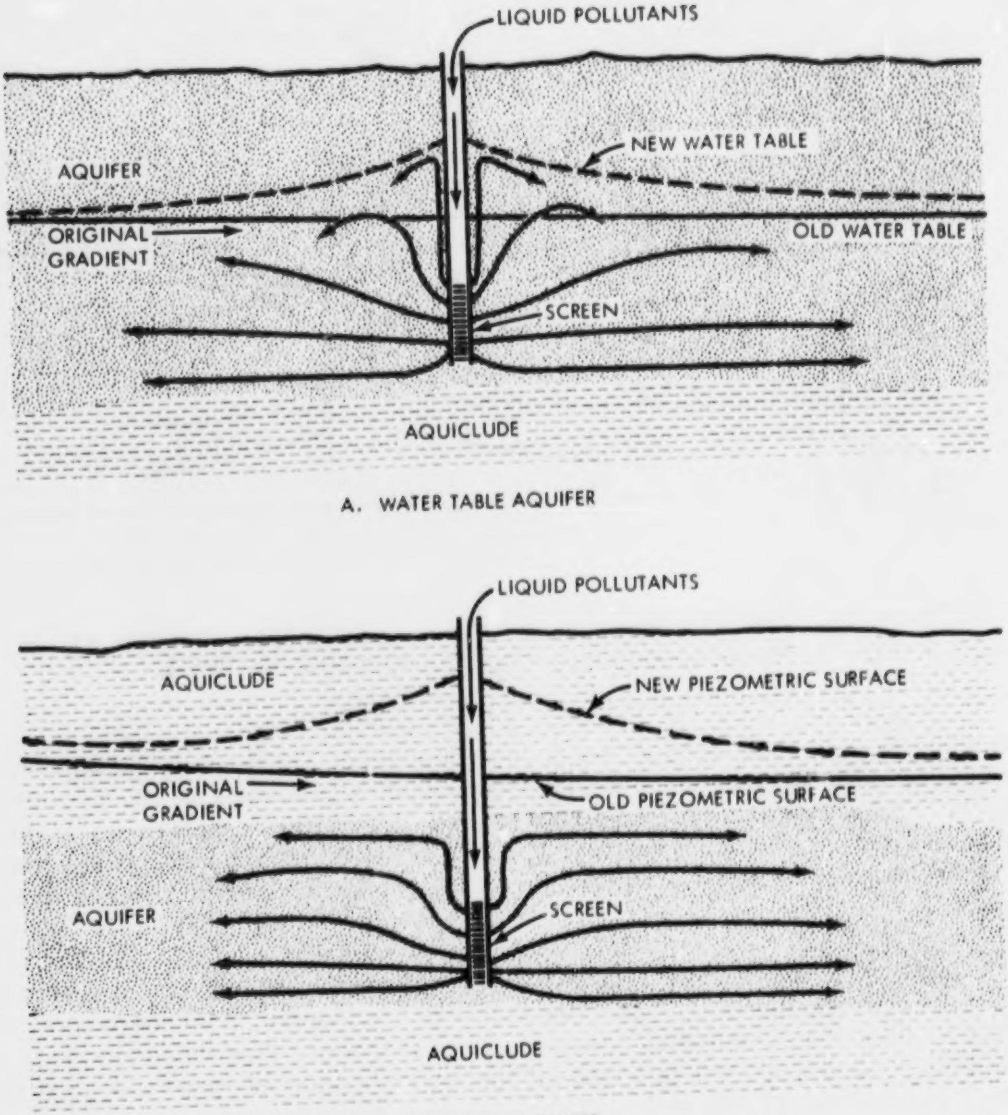

LIQUID POLLUTANTS
AQUIFER
NEW WATER TABLE
ORIGINAL GRADIENT
OLD WATER TABLE
SCREEN
AQUICLUDE
A. WATER TABLE AQUIFER
LIQUID POLLUTANTS
AQUICLUDE
NEW PIEZOMETRIC SURFACE
ORIGINAL GRADIENT
OLD PIEZOMETRIC SURFACE
AQUIFER
SCREEN
AQUICLUDE
B. ARTESIAN AQUIFER

Figure 35. Diagrams showing spread of pollutants injected through wells into water table and artesian aquifers (modified after Deutsch, 1963).

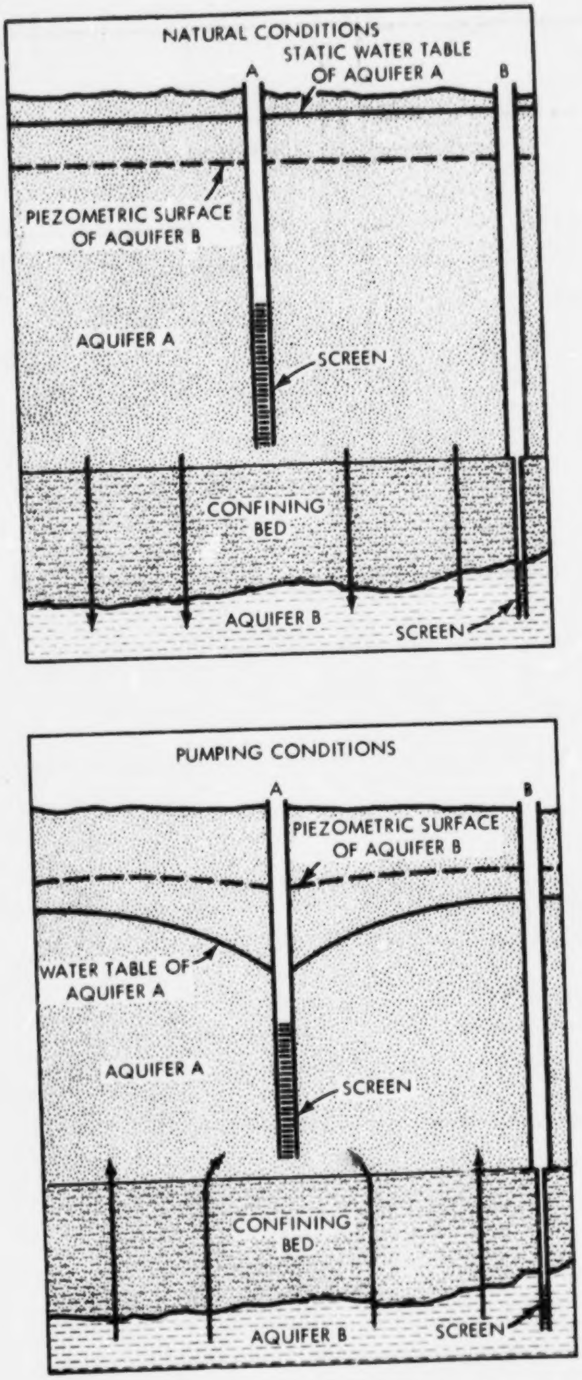
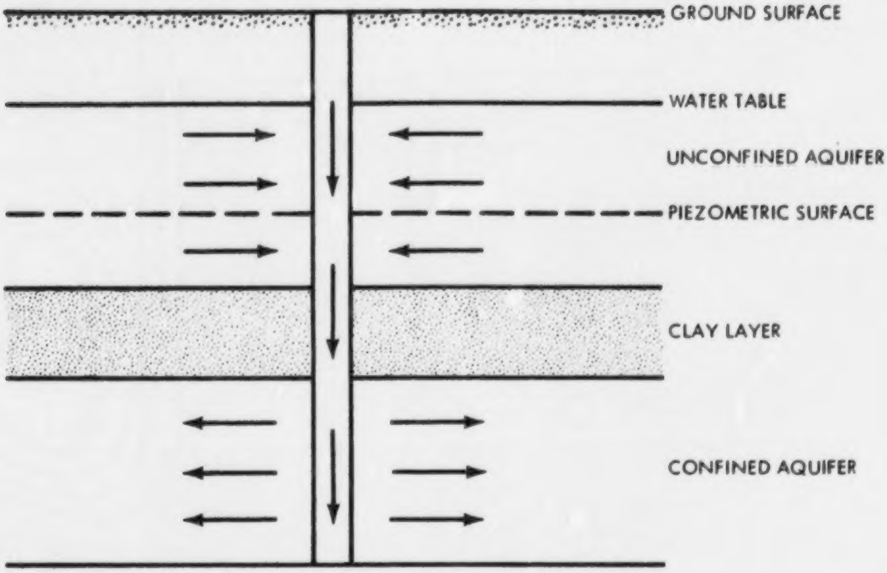
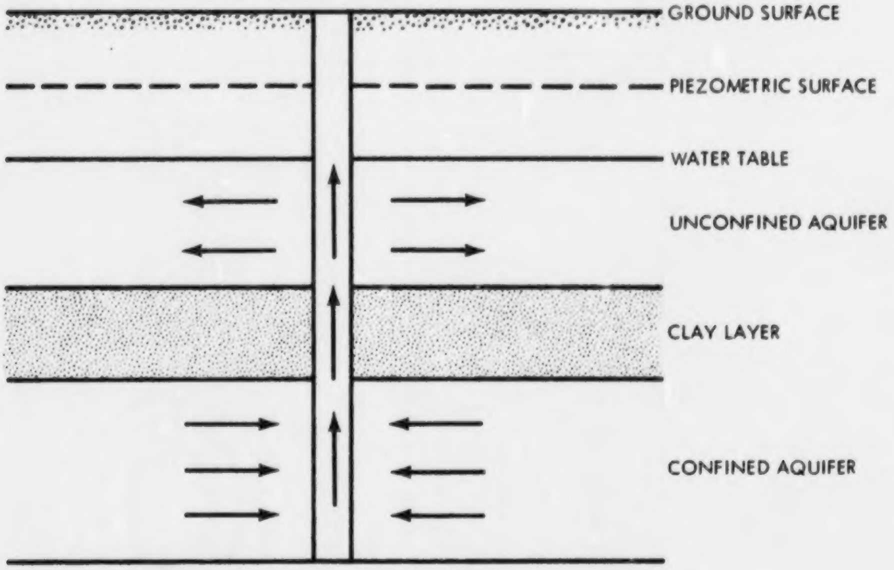

NATURAL CONDITIONS
STATIC WATER TABLE OF AQUIFER A
A
B
PIEZOMETRIC SURFACE OF AQUIFER B
AQUIFER A
SCREEN
CONFINING BED
AQUIFER B
SCREEN
PUMPING CONDITIONS
A
B
PIEZOMETRIC SURFACE OF AQUIFER B
WATER TABLE OF AQUIFER A
AQUIFER A
SCREEN
CONFINING BED
AQUIFER B
SCREEN

Figure 36. Diagrams showing reversal of aquifer leakage by pumping (Deutsch, 1963).


GROUND SURFACE
WATER TABLE
UNCONFINED AQUIFER
PIEZOMETRIC SURFACE
CLAY LAYER
CONFINED AQUIFER

(a) WATER TABLE ABOVE THE PIEZOMETRIC SURFACE


GROUND SURFACE
PIEZOMETRIC SURFACE
WATER TABLE
UNCONFINED AQUIFER
CLAY LAYER
CONFINED AQUIFER

(b) PIEZOMETRIC SURFACE ABOVE THE WATER TABLE

Figure 37. Diagrams showing aquifer leakage by vertical movement of water through a nonpumping well.

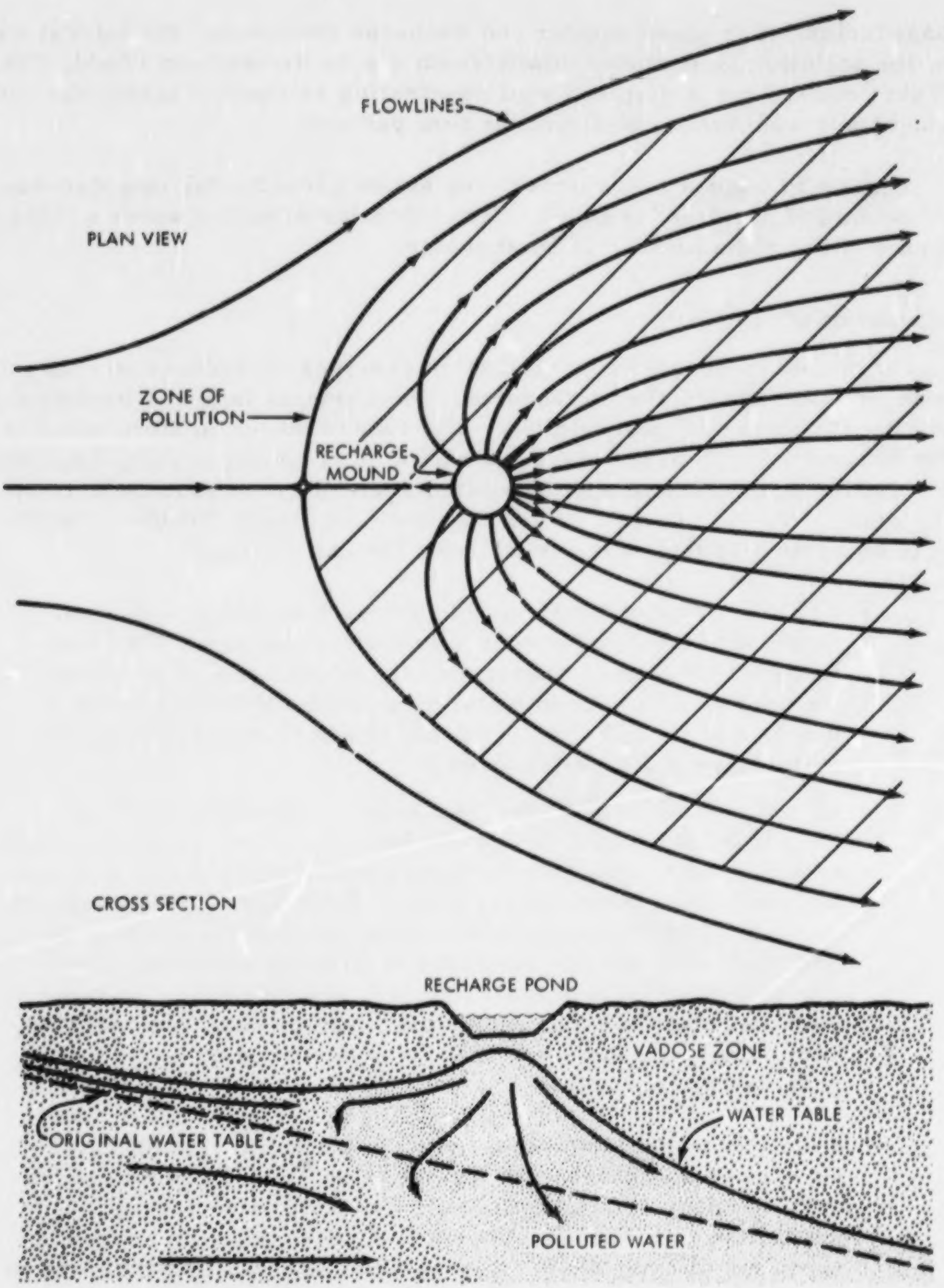

PLAN VIEW
FLOWLINES
ZONE OF POLLUTION
RECHARGE MOUND
CROSS SECTION
RECHARGE POND
VADOSE ZONE
WATER TABLE
ORIGINAL WATER TABLE
POLLUTED WATER

Figure 38. Diagrams showing lines of flow of pollutants from a recharge pond above a sloping water table (modified after Deutsch, 1963).

boundaries. For given aquifer and recharge conditions, the lateral spread of the pollution as it moves downstream can be determined (Todd, 1959). Waste water from a disposal well penetrating an aquifer having the same conditions would move in a similar flow pattern.

Figure 39 suggests how underlying saline groundwater can rise due to deepening of a stream channel. This intrusion of saline water occurs because of the reduced head of fresh water.

Attenuation of Pollution

Pollutants in groundwater tend to be removed or reduced in concentration with time and with distance traveled. Mechanisms involved include decay, chemical processes, and dilution. The rate of pollution attenuation is a function of the type of pollutant and of the local hydrogeologic framework. Predicting the degree to which pollutants will become attenuated is one of the most difficult, but also one of the most important, problems in the design of waste disposal systems utilizing the underground.

- DECAY. The reduction in the strength or potency of a pollutant with time constitutes a decay mechanism. This may involve oxidation of organic wastes in the zone of aeration, the decrease in concentration of a radioactive waste as a function of its half-life, or death of micro-organisms in unsuitable geologic environments.
- CHEMICAL PROCESSES. Adsorptive and other physical-chemical interfacial forces combine to remove pollutants from solution and to concentrate them on fine-grained soil and aquifer materials, particularly clays. Soils have a large capacity to adsorb organic materials. Many radioactive wastes, in addition, are strongly adsorbed by alluvial aquifers. Sorption may also include ion-exchange. Furthermore, cations such as potassium and ammonium, anions such as phosphate, and many trace elements tend to be adsorbed by soils and granular porous media.

  Salts can be precipitated from solution under certain conditions of temperature, pH, oxidation potential, and concentration. Thermodynamic relations can be used to determine if precipitation of mineral phases should be occurring under a given set of conditions. Anions most affected by precipitation are carbonate, bicarbonate, sulfate, and phosphate; cations most affected are calcium and magnesium.
- DILUTION. Pollutants in groundwater flowing through porous media tend to become diluted in concentration due to hydrodynamic dispersion. Microscopic dispersion is mixing caused

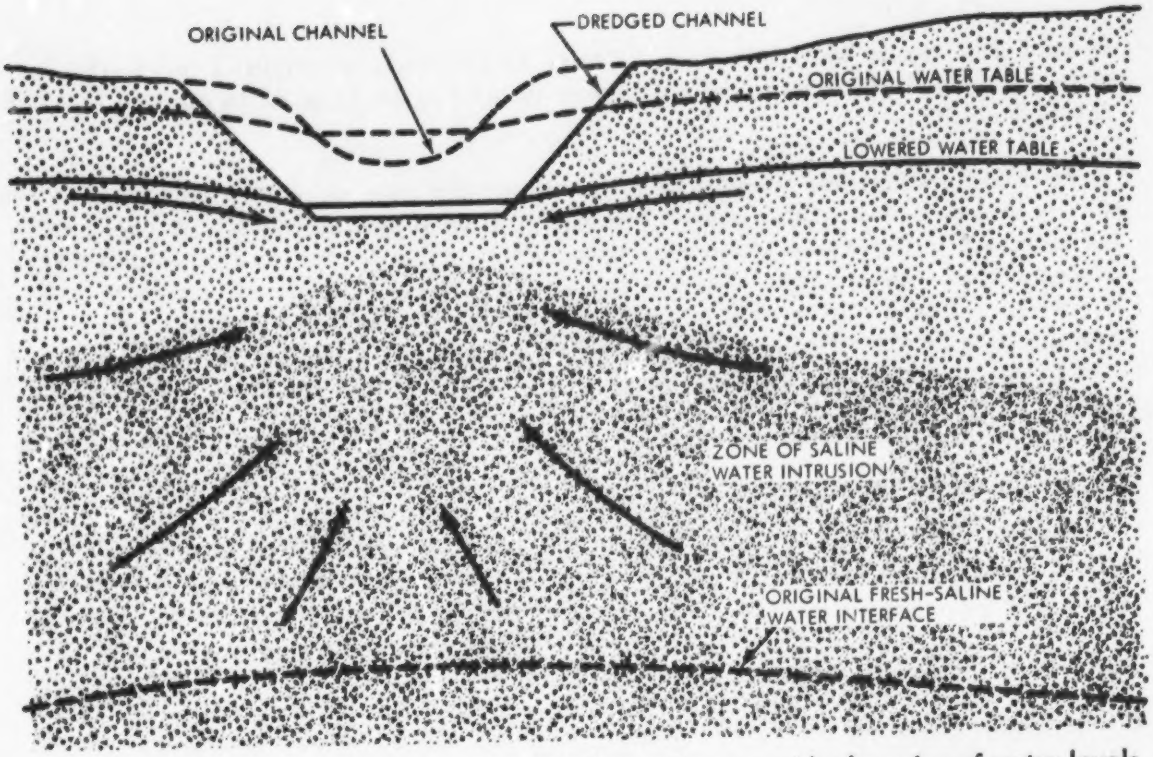

ORIGINAL CHANNEL
DREDGED CHANNEL
ORIGINAL WATER TABLE
LOWERED WATER TABLE
ZONE OF SALINE WATER INTRUSION
ORIGINAL FRESH-SALINE WATER INTERFACE

Figure 39. Diagram showing migration of saline water caused by lowering of water levels in a gaining stream.

by the tortuous flow around individual grains as water moves through an aquifer. Macroscopic dispersion is mixing resulting from heterogeneities of geologic formations, such as variable permeability, which cause flow lines to deviate and to converge. The result of these mechanisms is a longitudinal and lateral spreading of a pollutant within the groundwater so that the volume affected increases and the concentration decreases down-gradient. An analogous effect would be the dissipation of smoke from a smokestack as it drifts downwind in the atmosphere.

It is important to emphasize the role of aquifers in these attenuation processes. Aquifers composed of fine-grained materials possess very large surface areas which promote sorption processes. These same aquifers also encourage dilution by dispersion because of the large number of small interstices through which the groundwater must flow. On the other hand aquifers with large openings, whether from large-sized materials, cracks, or solution openings, permit a pollutant to advance rapidly underground with little or no reduction in concentration. Thus, in general, adsorption is greater in fine-grained aquifers, while dilution by mixing is greater in coarse-grained aquifers.

Specific statements cannot be made about the distances that pollution will travel because of the wide variability of aquifer conditions and types of pollutants. Yet certain generalizations which are widely applicable can be stated. For fine-grained alluvial aquifers, pollutants such as bacteria, viruses, organic materials, pesticides, and most radioactive materials, are usually removed by adsorption within distances of less than 100 meters. But most common ions in solution move unimpeded through these aquifers, subject only to dilution by mixing and chemical processes.

Distribution of Pollution Underground

Given the above attenuation processes, pollution from a point source moves outward until a harmless or very low concentration level is reached. Because each constituent of a pollution source may follow a different attenuation rate, the distance to which pollution is effective will vary with each quality component.

A hypothetical example of a waste-disposal site is shown in Figure 40. Here groundwater flows toward a river. Zones A, B, C, D, and E represent essentially stable limits for different contaminants resulting from the steady release of wastes of unchanging composition. Pollutants, once entrained in the saturated groundwater flow tend to form plumes (again analogous to smoke in the atmosphere) of polluted water extending downstream from the pollution source until they attenuate to some minimum quality levels. Only Zone E reaches the river in Figure 40 and is subsequently diluted by surface water.

The shape and size of a plume depends upon the local geology, the groundwater flow, the type and concentration of pollutant, the continuity of waste disposal, and any modifications of the groundwater system by man, such as well pumping (LeGrand, 1965b). Examples of various types of plumes are shown in Figure 41 and explained in Table 9. These are illustrative of the diversity of forms that plumes may assume. Where groundwater is moving relatively rapidly, a plume from a point source will tend to be long and thin; but where the flow rate is low, the pollutant will tend to spread more laterally to form a wider plume. Irregular plumes can be created by local influences such as pumping wells and nonuniformities in permeability.

Plumes ordinarily tend to become stable areas where there is a constant input of waste into the ground. This occurs for two reasons: the tendency

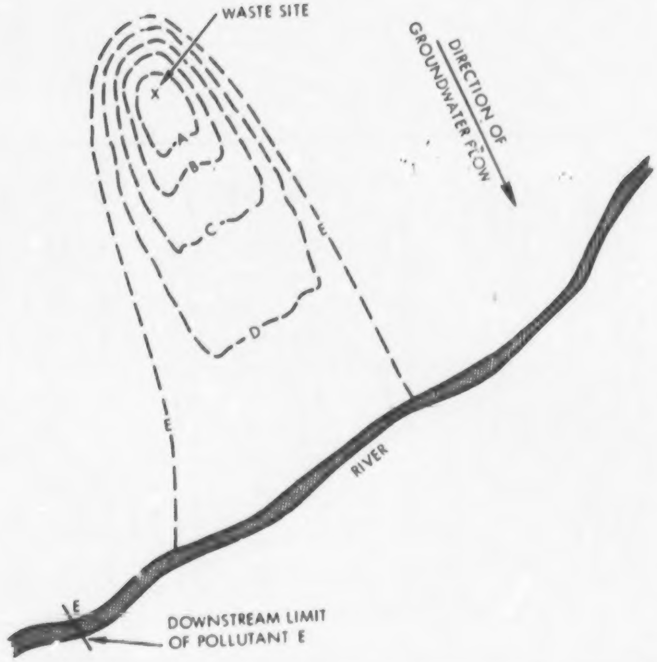

WASTE SITE
DIRECTION OF GROUNDWATER FLOW
X
A
B
C
D
E
E
RIVER
E
DOWNSTREAM LIMIT OF POLLUTANT E

Figure 40. Plan view of a water table aquifer showing the hypothetical areal extent to which specific pollutants of mixed wastes at a disposal site disperse and move to insignificant levels (modified after LeGrand, 1965b).

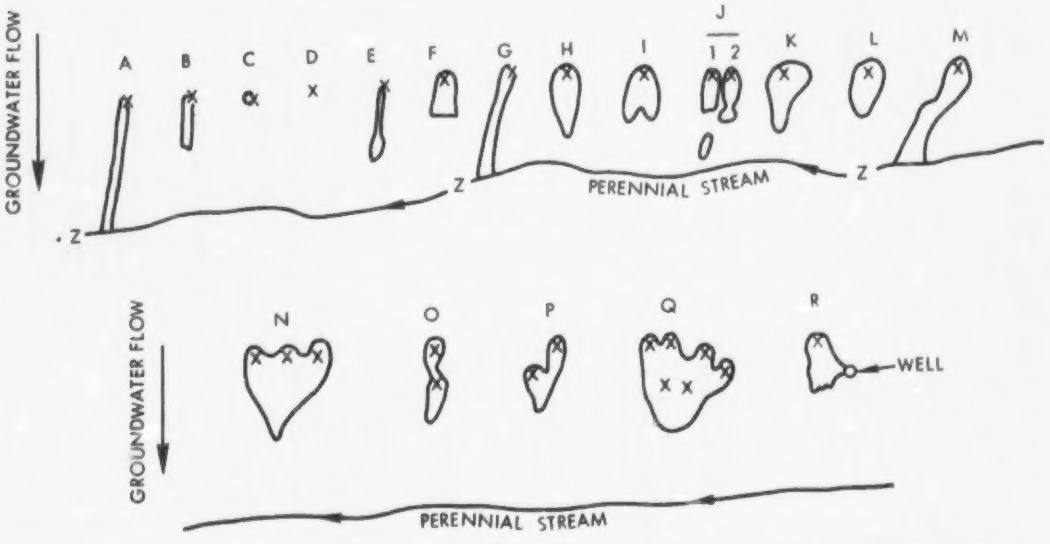
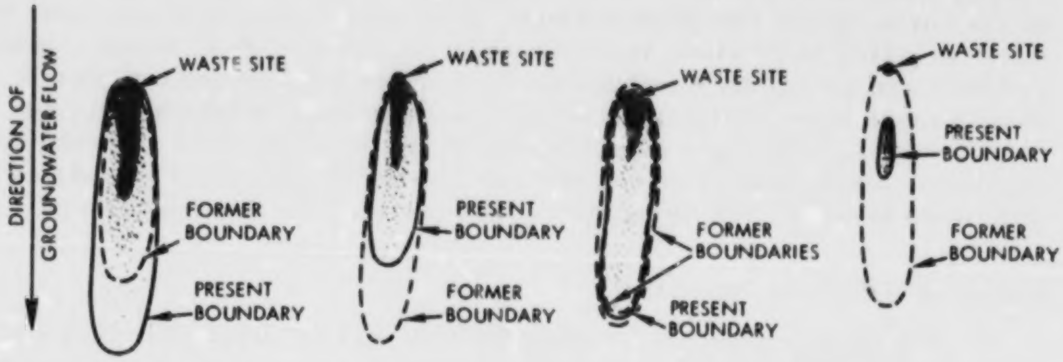

GROUNDWATER FLOW
A
B
C
D
E
F
G
H
I
J
1 2
K
L
M
Z
Z
Z
PERENNIAL STREAM
GROUNDWATER FLOW
N
O
P
Q
R
WELL
PERENNIAL STREAM

Figure 41. Types of pollution plumes in the upper part of the zone of saturation (plan view). An "X" marks the core of contamination beneath a waste site and "Z" the point downstream at which some plumes terminate (LeGrand, 1965b).

TABLE 9. EXPLANATION OF PLUMES SHOWN IN FIGURE 41 (modified after LeGrand, 1965b)

Plume Governed By				Liquid Waste Recharge Forming Water-Table Mound	Composite Water Sites	Examples of Types of Pollutant	Remarks
Site	Dilution	Decay	Sorption				
A	Not appreciable in ground; some in streams	No	No	No	No	Chlorides, nitrates	
B	Not appreciable	Either decay or sorption or both		No	No	---	
C	Improbable	Perhaps	Perhaps	No	No	Sewage, radioactive wastes	Probably small waste release or good attenuation in zone of aeration.
D	No malenclave formed (See Remarks)	Either decay or sorption or both		No	No	Sewage, radioactive wastes	Pollutant is completely attenuated in zone of aeration and does not reach zone of saturation.
E	Slight near waste site; some at greater distance	Possibly	Possibly	No	No	---	Lack of dispersion near waste site typical of linear openings in rock; polluted water downgradient disperses into different type of material.
F	Yes; suggestive of nearly homogeneous porous materials	Improbable	Improbable	No	No	Chlorides, nitrates	
G	Not appreciable in ground; some near and in stream	Not appreciable	Not appreciable	No	No	Chlorides, nitrates	Irregularities in permeability cause deviation in plume.
H	Yes; suggestive of nearly homogeneous porous materials	Probably either decay or sorption or both		No	No	Sewage, radioactive wastes	
I	Yes	Perhaps	Perhaps	No	No	---	Downgradient split in plume may be due to dense impermeable rock or great increase in sorptive materials.
J	Slight	Not appreciable	Probably not appreciable	No	No	Chlorides, nitrates	Downgradient plume is due to shunting of pollutant to land surface at tail of upper plume and reinfiltration of pollutant.
K	Yes; suggestive of nearly homogeneous porous materials	Either decay or sorption or both		Yes	No	Sewage, radioactive wastes	Irregularities in plume caused by changes in permeability and/or sorption.
L	Yes; suggestive of nearly homogeneous porous materials	Either decay or sorption or both		Yes	No	Sewage, radioactive wastes	
M	Some in ground and stream	Not appreciable	Not appreciable	Yes		Chlorides, nitrates	Deviation in plume due to impermeable zone.
N	Yes	Either decay or sorption or both		Yes	No	Sewage, radioactive wastes	Polluted water from three waste sites at right angles to groundwater flow, merging to form a composite plume.
O	Yes	Either decay or sorption or both		No	Yes	Sewage, radioactive wastes	Polluted water from two waste sites parallel to groundwater flow, forming a composite site.
P	Some	Either decay or sorption or both		No	Yes	Sewage, radioactive wastes	Polluted water from two waste sites at an angle with groundwater flow, forming a composite plume.
Q	Some	Either decay or sorption or both		No	Yes	Sewage, radioactive wastes	Large composite plume formed by several waste sites.
R	Yes	Either decay or sorption or both		No	No	Sewage, radioactive wastes	Pumping well draws plume toward it; polluted water is greatly diluted at the well.


DIRECTION OF GROUNDWATER FLOW
WASTE SITE
FORMER BOUNDARY
PRESENT BOUNDARY
WASTE SITE
PRESENT BOUNDARY
FORMER BOUNDARY
WASTE SITE
FORMER BOUNDARIES
PRESENT BOUNDARY
WASTE SITE
PRESENT BOUNDARY
FORMER BOUNDARY

ENLARGING PLUME

1. INCREASE IN RATE OF DISCHARGED WASTES
2. SORPTION ACTIVITY USED UP
3. EFFECTS OF CHANGES IN WATER TABLE

REDUCING PLUME

1. REDUCTION IN WASTES
2. EFFECTS OF CHANGES IN WATER TABLE
    a. MORE EFFECTIVE SORPTION
    b. MORE EFFECTIVE DILUTION
    c. SLOWER MOVEMENT AND MORE TIME FOR DECAY

NEARLY STABLE PLUME

1. ESSENTIALLY SAME WASTE INPUT
2. SORPTION CAPACITY NOT FULLY UTILIZED
3. DILUTION EFFECT FAIRLY STABLE
4. SLIGHT WATER TABLE FLUCTUATION OR EFFECTS OF WATER TABLE FLUCTUATION NOT IMPORTANT

SHRUNKEN PLUME

1. WASTE NO LONGER DISPOSED AND NO LONGER LEACHED AT ABANDONED WASTE SITE

Figure 42. Changes in plumes and factors causing the changes (modified after LeGrand, 1965a).

for enlargement as pollutants continue to be added at a point source is counterbalanced by the combined attenuation mechanisms, or the pollutant reaches a location of groundwater discharge, such as a stream, and emerges from the underground. When a waste is first released into groundwater, the plume expands until a quasi-equilibrium stage is reached. If sorption is important, a steady inflow of pollution will cause a slow expansion of the plume as the earth materials within it reach a sorption capability limit.

An approximately stable plume will expand or contract generally in response to changes in the rate of waste discharge. Figure 42 shows changes in plumes that can be anticipated from variations in waste inputs.

An important aspect of groundwater pollution is the fact that it may persist underground for years, decades, or even centuries. This is in marked contrast to surface water pollution. The average residence time of groundwater is on the order of 200 years; consequently, a pollutant which is not readily decayed or sorbed underground can remain as a degrading influence on the resource for indefinite periods. The comparable residence time for water in a stream or river is on the order of 10 days; thus, surface water pollution can be rapidly eliminated. Reclaiming polluted groundwater is usually much more difficult and time consuming than reclaiming polluted surface water. Underground pollution control is usually best achieved by regulating the pollution source, and secondarily by physically entrapping and, when feasible, removing the polluted water from the underground.

Evaluation of Pollution Potential

To provide guidance in evaluating the potential pollution of a given site, LeGrand (1964) developed an empirical point-count system. The concept is applicable to locations of waste disposal sites and to wells; water table aquifer conditions are presumed.

Local factors influencing pollution include:

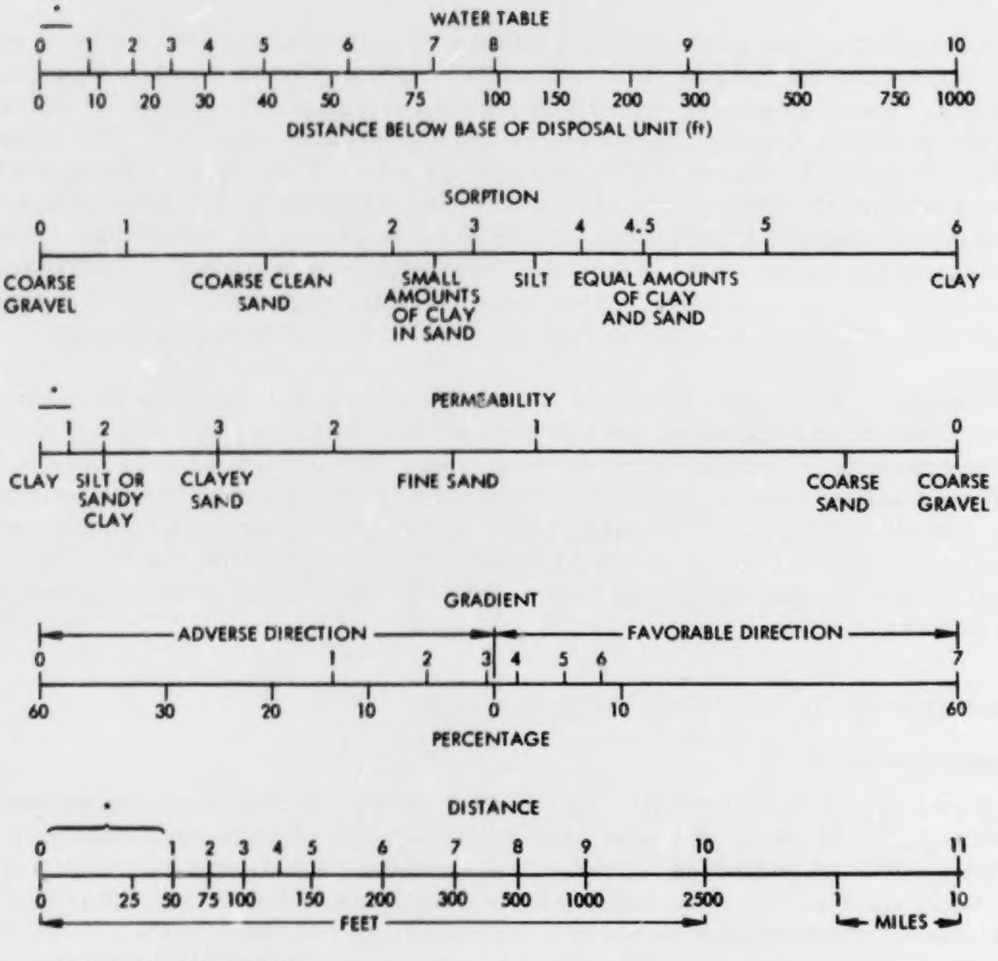
- Depth to water table
- Sorption
- Permeability
- Water table gradient
- Distance.

The rating chart shown in Figure 43 illustrates the evaluation procedure for sites in unconsolidated alluvial materials. A numerical value is read above the line for each of the five factors based upon the corresponding data below the line.

The pollution potential of a given site is the sum of the numerical ratings of the five factors in Figure 43. Total point values may be interpreted in terms of possibility of pollution as follows:

Total Points	Possibility of Pollution
0-4	Imminent
4-8	Probable or possible
8-12	Possible but not likely
12-25	Very improbable
25-35	Impossible

LeGrand (1964) emphasized that his index system for evaluating pollution was imperfect and only a beginning. Certainly refinements can and should be made in the future, but for the present his approach is useful and sound.



*UNACCEPTABLE RANGES

Figure 43. Rating chart for pollution potential in unconfined aquifers of unconsolidated alluvial materials (modified after LeGrand, 1964).

Trends in Groundwater Pollution

Because of the many millions of groundwater pollution sources in the United States, comprehensive data defining the extent of the problem are almost nonexistent. Thus, although an overview of the magnitude of the problem is difficult to obtain, basic trends of pollution can be suggested from a demographic approach.

Recognizing that groundwater pollution results from activities of man, one can relate the magnitude of pollution to population and other demographic factors. As an example, Figure 44 shows the estimated growth of underground pollution for the United States during the 20th century. The ordinate is the percent of current (1974) pollution levels. The curve preceding 1974 is based upon the growth of urban population adjusted by a factor of two to account for industrial development, increased per capita water use, development of irrigated agriculture, and introduction of agricultural fertilizers since 1900. The cumulative aspect of pollution, whereby pollution dating from say 1954 may still be underground in 1974, has been neglected.

The curve in Figure 44 has been extended from 1974 to 2000 based on estimated urban population growth only without adjustment. What this analysis suggests is a tenfold increase in groundwater pollution from 1900 to the present, and — assuming no future efforts to control groundwater pollution — a further 60 percent increase by the end of the century. Hopefully, with the implementation of the Federal Water Pollution Control Act of 1972 (PL 92-500) and the Safe Drinking Water Act (PL 93-523) this dire forecast will not become reality.

CONSTITUENTS IN POLLUTED GROUNDWATER

Quality Categories

Water quality is normally expressed in terms of four basic categories: chemical, biological, physical, and radiological. Within each category a large number of individual parameters and constituents can be identified. Table 10 lists a wide range of possible pollutants which may be found by analysis of groundwater samples. The possible potential pollutants in the chemical and biological categories are, of course, virtually limitless. On the other hand most analyses of groundwater include only a few key parameters and constituents because they are sufficient to serve as indicators of pollution.

Effects of Water Use

The sources and causes of groundwater pollution are by definition related to man's use of water. The diversity of impacts of man's activities on the hydrologic cycle create a complex and interrelated series of modifications to natural water quality. The sources of water and the effects of man on

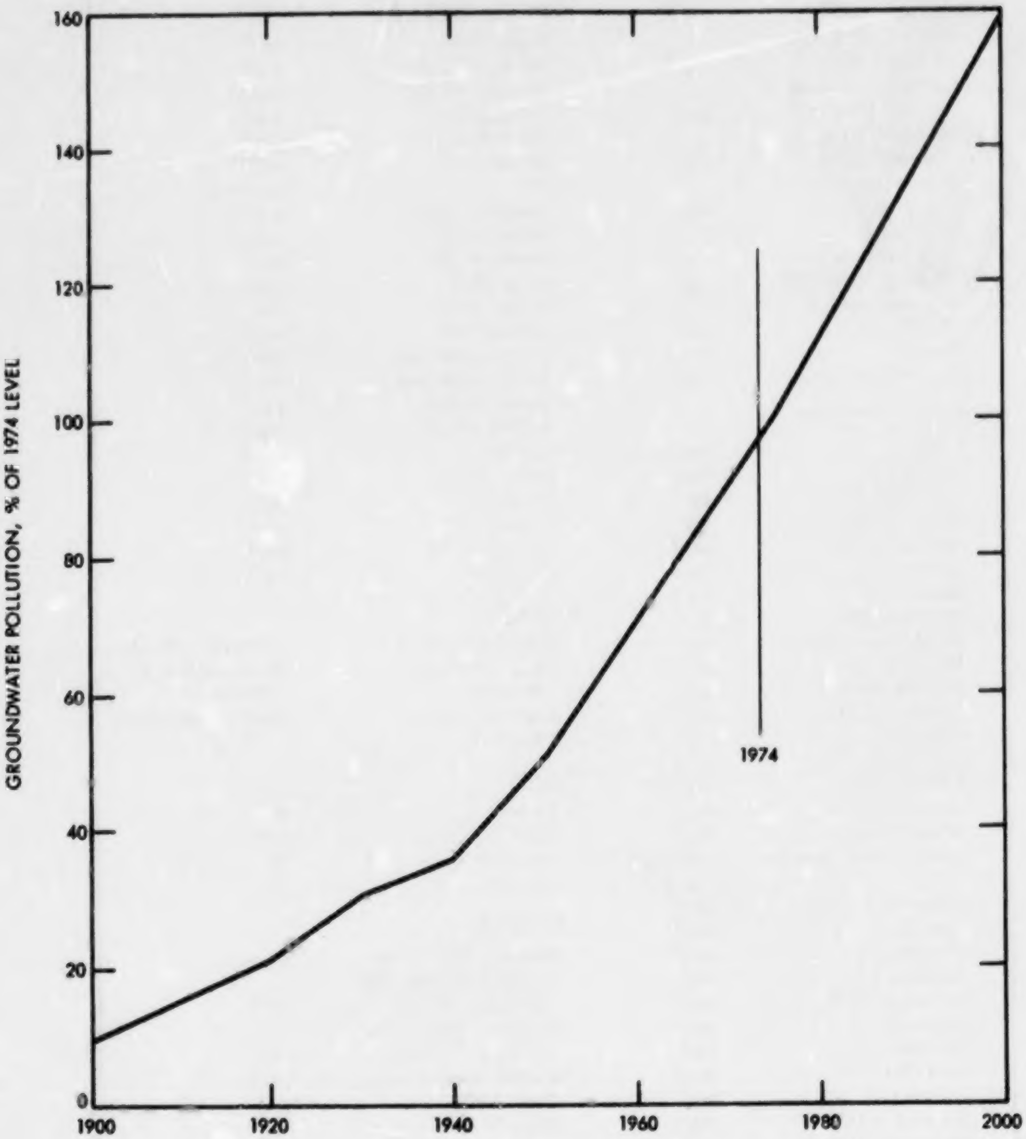


Figure 44. Estimated trend of groundwater pollution in the United States during the 20th Century.

TABLE 10. PARAMETERS AND CONSTITUENTS WHICH MAY BE INCLUDED IN ANALYSES OF GROUNDWATER QUALITY*

Chemical - Organic	Units
Biochemical Oxygen Demand (BOD)	mg/l
Carbon Chloroform Extract (CCE)	µg/l
Chemical Oxygen Demand (COD)	mg/l
Chlorinated Phenoxy Acid Herbicides	µg/l
Detergents (Surfactants)	mg/l
Organic Carbon (C)	mg/l
Organophosphorus Pesticides	µg/l
Phenols	mg/l
Tannins and Lignins	mg/l
Chemical - Inorganic	
Acidity	mg/l
Alkalinity	mg/l
Aluminum (Al)	µg/l
Ammonia (NH_4)	mg/l
Antimony (Sb)	µg/l
Arsenic (As)	µg/l
Barium (Ba)	µg/l
Beryllium (Be)	µg/l
Bicarbonate (HCO_3)	mg/l
Boron (B)	µg/l
Bromide (Br)	µg/l
Cadmium (Cd)	µg/l
Calcium (Ca)	mg/l
Carbonate (CO_3)	mg/l
Chloride (Cl)	mg/l
Chromium (Cr)	µg/l
Cobalt (Co)	µg/l
Conductance, specific	umhos/cm at 25°C
Copper (Cu)	µg/l
Cyanide (CN)	µg/l
Fluoride (F)	µg/l
Hardness	mg/l
Hydroxide (OH)	mg/l
Iodide (I)	µg/l
Iron (Fe)	ug/l
Lead (Pb)	µg/l
Lithium (Li)	µg/l
Magnesium (Mg)	mg/l
Manganese (Mn)	ug/l
Mercury (Hg)	ug/l
Molybdenum (Mo)	ug/l

Chemical - Inorganic	Units
Nickel (Ni)	µg/l
Nitrite (NO_2)	mg/l
Nitrate (NO_3)	mg/l
Nitrogen (N)	mg/l
Oil and Grease	mg/l
Oxygen (O_2)	mg/l
pH	pH units
Phosphate (PO_4)	mg/l
Potassium (K)	mg/l
Selenium (Se)	µg/l
Silver (Ag)	µg/l
Silica (SiO_2)	mg/l
Sodium (Na)	mg/l
Solids, dissolved	mg/l
Solids, suspended	mg/l
Strontium (Sr)	µg/l
Sulfate (SO_4)	mg/l
Sulfide (S)	mg/l
Sulfite (SO_3)	mg/l
Tin (Sn)	µg/l
Titanium (Ti)	µg/l
Vanadium (V)	µg/l
Zinc (Zn)	µg/l
Biological	
Coliform Bacteria	Coliforms/100 ml
Fecal Coliform Bacteria	Fecal Coliforms/ 100 ml
Fecal Streptococci Bacteria	Fecal Streptococci/ 100 ml
Physical	
Color	PCU
Odor	TO
Temperature	°C
Turbidity	TU
Radiological	
Barium - 140 (^{140}Ba)	pc/l
Cerium - 141 and 144 (^{141}Ce, ^{144}Ce)	pc/l
Cesium - 134 and 137 (^{134}Cs, ^{137}Cw)	pc/l
Gamma Spectrometry	pc/l
Gross Alpha	pc/l
Gross Gamma	nc/l
Iodine - 131(^{131}I)	pc/l
Neptunium - 239(^{239}Np)	pc/l
Radium (Ra)	pc/l
Thorium (Th)	µg/l
Tritium (^3H)	pc/l
Uranium (U)	µg/l

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*This list is illustrative rather than comprehensive. Various ionic forms of some constituents as well as different analytic expressions for certain constituents have not been included.

water quality are suggested in the water quality cycle of Figure 45. Note that there are four main uses of water — agricultural, industrial, commercial, and domestic; each of these in turn exerts an influence on groundwater quality.

AGRICULTURAL USES. The various agricultural uses of water and their effects on water quality are shown schematically in Figure 46. Chemical constituents from agricultural activities are added at the land surface, as it moves downward through the soil, and as it passes through disposal sites for solid agricultural wastes. In particular, irrigation degrades the quality of water due to evapotranspiration, which concentrates salts in irrigation return water. Addition of fertilizers, soil amendments, pesticides, and other additives applied to the soil also contribute to groundwater pollution.

Solid wastes produced by agricultural activities, particularly dairies and feedlots, are in part deposited in sanitary landfills. Leachates and gases generated by the decomposition of solid wastes may affect the quality. The effect and the areal extent of such leachates vary depending upon the volume of leachate, the rate of mixing with groundwater, the volume of groundwater available, and the rate of groundwater movement.

INDUSTRIAL USES. The major uses of water in industrial plants are for cooling, manufacturing and processing, and sanitation.

Figure 47 shows industrial uses of water and their effects on water quality. As could be expected, the quality of waste water varies with respect to the type of industry and water use.

Water cooling systems vary from "open once-through" to "closed recirculating." The first method requires large volumes of water, and waste water is disposed of after one use; a closed recirculating system uses less water but generates wastes with higher salinities. Softening of water before use in cooling, to inhibit scale formation, results in generation of brine wastes. Water returned to the underground after use for cooling will possess a higher salt content and a higher temperature.

Boiler feed systems have similar "open" and "closed" designs and yield waste waters with increased salinities and temperatures. Industrial organic wastes other than sewage generally possess a higher COD than domestic wastes. Nonreclaimable industrial waste water may be disposed into deep injection wells, whereas reclaimable waste water may be artificially recharged to groundwater after treatment.

COMMERCIAL USES. Figure 48 diagrams commercial uses of water and their effects on water quality. Outside water use includes irrigation of lawns, shrubs, and landscaping as well as activities such as car washes.

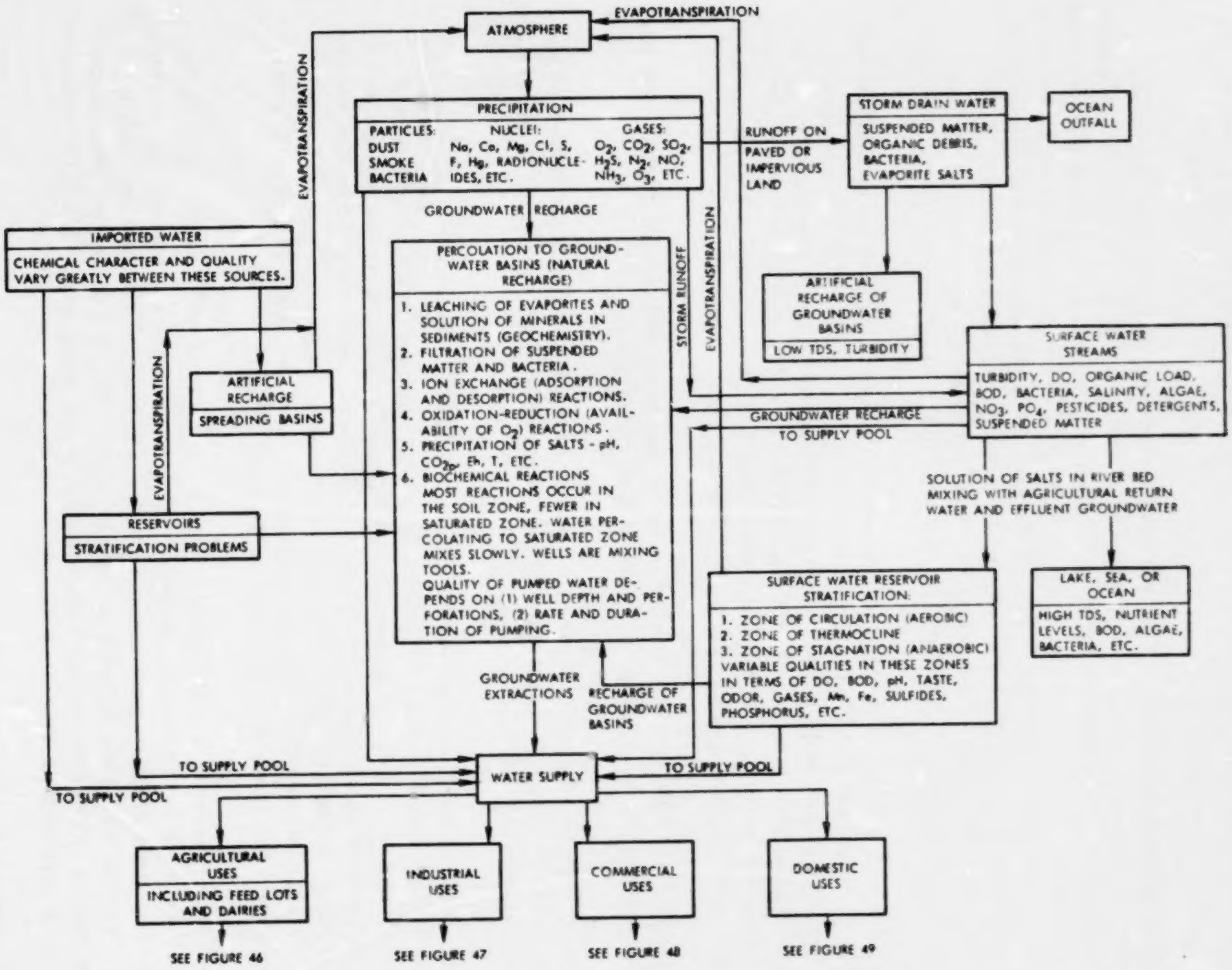
ATMOSPHERE
EVAPOTRANSPIRATION
EVAPOTRANSPIRATION
PRECIPITATION
PARTICLES: DUST SMOKE BACTERIA
NUCLEI: Na, Ca, Mg, Cl, S, F, Hg, RADIONUCLEIDES, ETC.
GASES: O2, CO2, SO2, H2S, N2, NO, NH3, O3, ETC.
RUNOFF ON PAVED OR IMPERVIOUS LAND
STORM DRAIN WATER
SUSPENDED MATTER, ORGANIC DEBRIS, BACTERIA, EVAPORITE SALTS
OCEAN OUTFALL
IMPORTED WATER
CHEMICAL CHARACTER AND QUALITY VARY GREATLY BETWEEN THESE SOURCES.
GROUNDWATER RECHARGE
PERCOLATION TO GROUNDWATER BASINS (NATURAL RECHARGE)
1. LEACHING OF EVAPORITES AND SOLUTION OF MINERALS IN SEDIMENTS (GEOCHEMISTRY).
2. FILTRATION OF SUSPENDED MATTER AND BACTERIA.
3. ION EXCHANGE (ADSORPTION AND DESORPTION) REACTIONS.
4. OXIDATION-REDUCTION (AVAILABILITY OF O2) REACTIONS.
5. PRECIPITATION OF SALTS - pH, CO2p, Eh, T, ETC.
6. BIOCHEMICAL REACTIONS
MOST REACTIONS OCCUR IN THE SOIL ZONE, FEWER IN SATURATED ZONE. WATER PERCOLATING TO SATURATED ZONE MIXES SLOWLY. WELLS ARE MIXING TOOLS.
QUALITY OF PUMPED WATER DEPENDS ON (1) WELL DEPTH AND PERFORATIONS, (2) RATE AND DURATION OF PUMPING.
STORM RUNOFF
EVAPOTRANSPIRATION
ARTIFICIAL RECHARGE OF GROUNDWATER BASINS
LOW TDS, TURBIDITY
ARTIFICIAL RECHARGE
SPREADING BASINS
EVAPOTRANSPIRATION
SURFACE WATER STREAMS
TURBIDITY, DO, ORGANIC LOAD, BOD, BACTERIA, SALINITY, ALGAE, NO3, PO4, PESTICIDES, DETERGENTS, SUSPENDED MATTER
GROUNDWATER RECHARGE
TO SUPPLY POOL
SOLUTION OF SALTS IN RIVER BED MIXING WITH AGRICULTURAL RETURN WATER AND EFFLUENT GROUNDWATER
RESERVOIRS
STRATIFICATION PROBLEMS
SURFACE WATER RESERVOIR STRATIFICATION:
1. ZONE OF CIRCULATION (AEROBIC)
2. ZONE OF THERMOCLINE
3. ZONE OF STAGNATION (ANAEROBIC)
VARIABLE QUALITIES IN THESE ZONES IN TERMS OF DO, BOD, pH, TASTE, ODOR, GASES, Mn, Fe, SULFIDES, PHOSPHORUS, ETC.
LAKE, SEA, OR OCEAN
HIGH TDS, NUTRIENT LEVELS, BOD, ALGAE, BACTERIA, ETC.
GROUNDWATER EXTRACTIONS
RECHARGE OF GROUNDWATER BASINS
TO SUPPLY POOL
TO SUPPLY POOL
TO SUPPLY POOL
WATER SUPPLY
AGRICULTURAL USES
INCLUDING FEED LOTS AND DAIRIES
INDUSTRIAL USES
COMMERCIAL USES
DOMESTIC USES
SEE FIGURE 46
SEE FIGURE 47
SEE FIGURE 48
SEE FIGURE 49

Figure 45. Water quality cycle — sources and uses of water and effects on water quality (modified after Hassan, 1974).

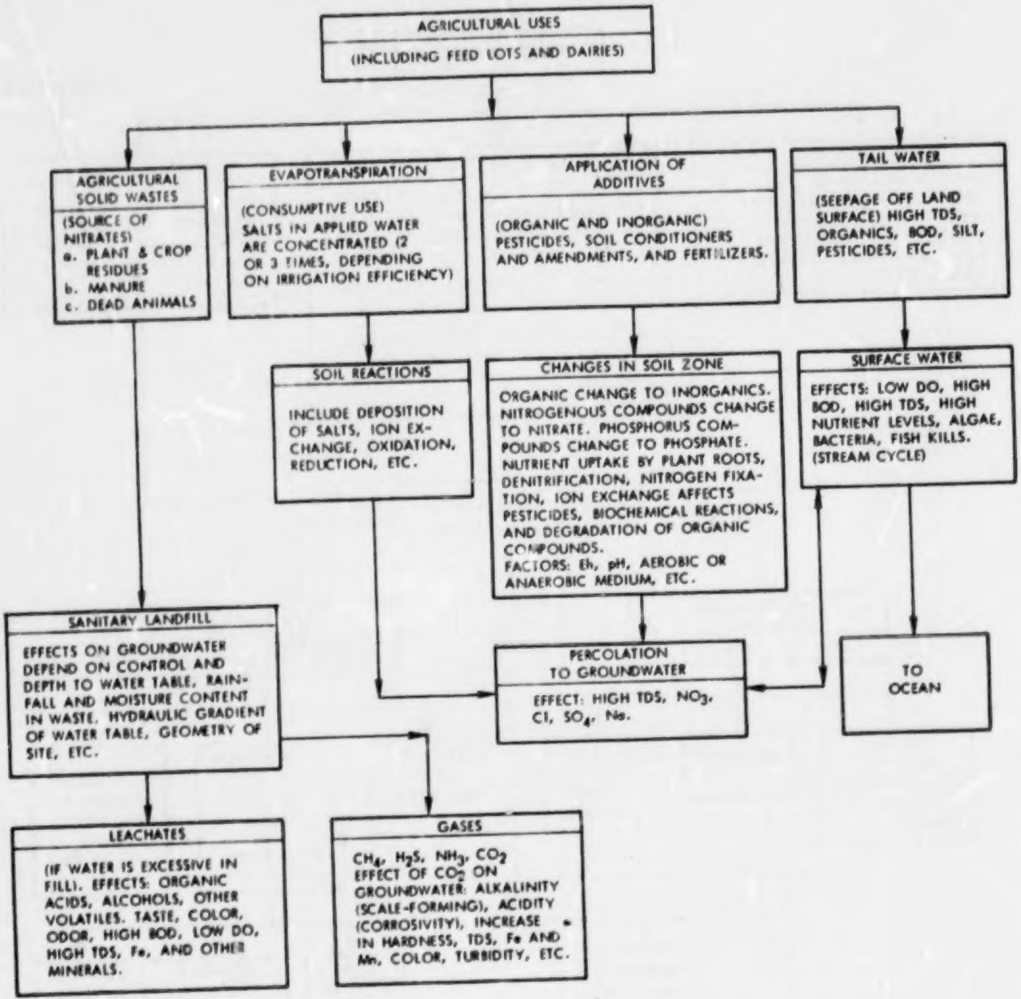
AGRICULTURAL USES
(INCLUDING FEED LOTS AND DAIRIES)
AGRICULTURAL SOLID WASTES
(SOURCE OF NITRATES) a. PLANT & CROP RESIDUES b. MANURE c. DEAD ANIMALS
EVAPOTRANSPIRATION
(CONSUMPTIVE USE) SALTS IN APPLIED WATER ARE CONCENTRATED (2 OR 3 TIMES, DEPENDING ON IRRIGATION EFFICIENCY)
APPLICATION OF ADDITIVES
(ORGANIC AND INORGANIC) PESTICIDES, SOIL CONDITIONERS AND AMENDMENTS, AND FERTILIZERS.
TAIL WATER
(SEEPAGE OFF LAND SURFACE) HIGH TDS, ORGANICS, BOD, SILT, PESTICIDES, ETC.
SOIL REACTIONS
INCLUDE DEPOSITION OF SALTS, ION EXCHANGE, OXIDATION, REDUCTION, ETC.
CHANGES IN SOIL ZONE
ORGANIC CHANGE TO INORGANICS. NITROGENOUS COMPOUNDS CHANGE TO NITRATE. PHOSPHORUS COMPOUNDS CHANGE TO PHOSPHATE. NUTRIENT UPTAKE BY PLANT ROOTS, DENITRIFICATION, NITROGEN FIXATION, ION EXCHANGE AFFECTS PESTICIDES, BIOCHEMICAL REACTIONS, AND DEGRADATION OF ORGANIC COMPOUNDS.
FACTORS: Eh, pH, AEROBIC OR ANAEROBIC MEDIUM, ETC.
SURFACE WATER
EFFECTS: LOW DO, HIGH BOD, HIGH TDS, HIGH NUTRIENT LEVELS, ALGAE, BACTERIA, FISH KILLS. (STREAM CYCLE)
SANITARY LANDFILL
EFFECTS ON GROUNDWATER DEPEND ON CONTROL AND DEPTH TO WATER TABLE, RAINFALL AND MOISTURE CONTENT IN WASTE. HYDRAULIC GRADIENT OF WATER TABLE, GEOMETRY OF SITE, ETC.
PERCOLATION TO GROUNDWATER
EFFECT: HIGH TDS, NO_3, Cl, SO_4, Na.
TO OCEAN
LEACHATES
(IF WATER IS EXCESSIVE IN FILL). EFFECTS: ORGANIC ACIDS, ALCOHOLS, OTHER VOLATILES. TASTE, COLOR, ODOR, HIGH BOD, LOW DO, HIGH TDS, Fe, AND OTHER MINERALS.
GASES
CH_4, H_2S, NH_3, CO_2
EFFECT OF CO_2 ON GROUNDWATER: ALKALINITY (SCALE-FORMING), ACIDITY (CORROSIVITY), INCREASE IN HARDNESS, TDS, Fe AND Mn, COLOR, TURBIDITY, ETC.

Figure 46. Agricultural uses of water and their effects on water quality (modified after Hassan, 1974).

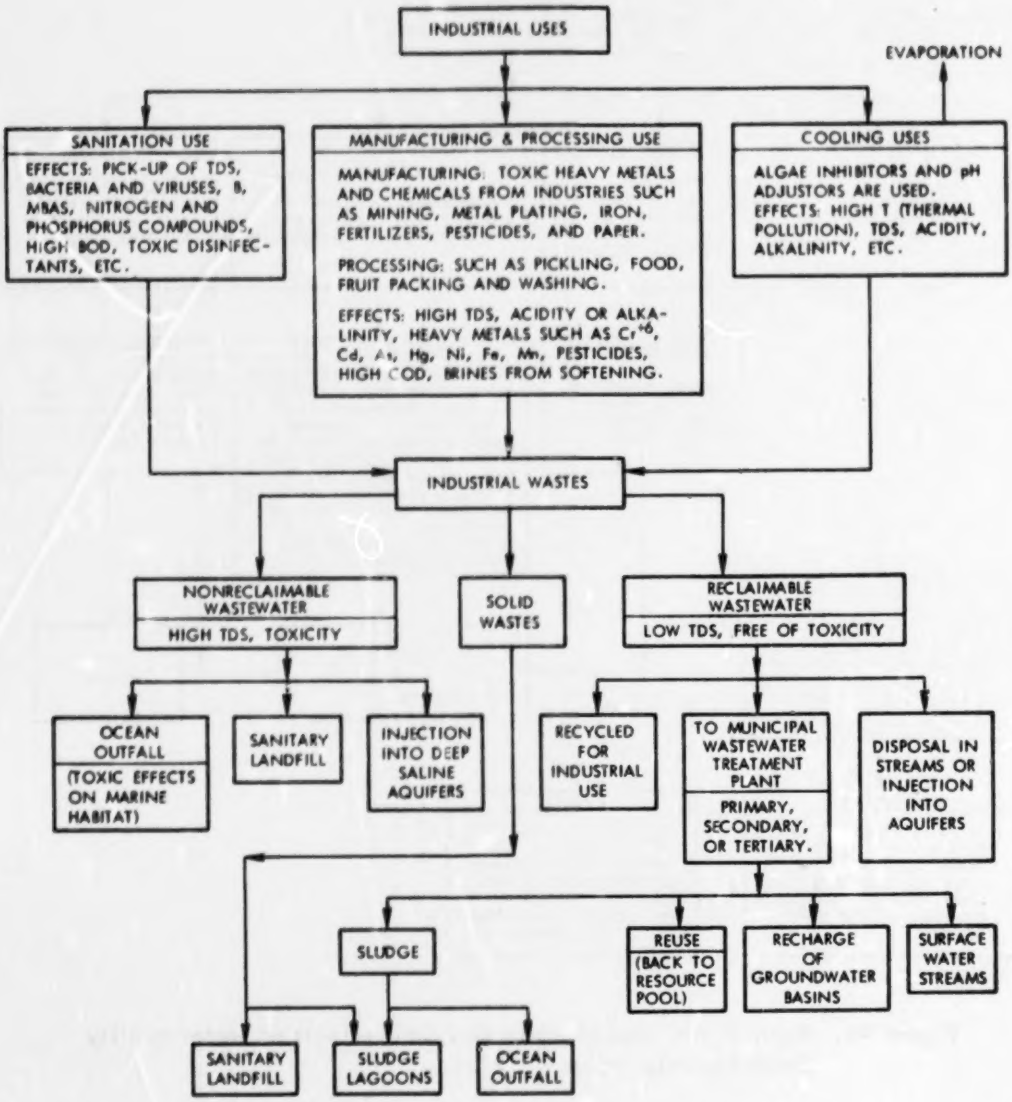
INDUSTRIAL USES
EVAPORATION
SANITATION USE
EFFECTS: PICK-UP OF TDS, BACTERIA AND VIRUSES, B, MBAS, NITROGEN AND PHOSPHORUS COMPOUNDS, HIGH BOD, TOXIC DISINFECTANTS, ETC.
MANUFACTURING & PROCESSING USE
MANUFACTURING: TOXIC HEAVY METALS AND CHEMICALS FROM INDUSTRIES SUCH AS MINING, METAL PLATING, IRON, FERTILIZERS, PESTICIDES, AND PAPER.
PROCESSING: SUCH AS PICKLING, FOOD, FRUIT PACKING AND WASHING.
EFFECTS: HIGH TDS, ACIDITY OR ALKALINITY, HEAVY METALS SUCH AS Cr+6, Cd, As, Hg, Ni, Fe, Mn, PESTICIDES, HIGH COD, BRINES FROM SOFTENING.
COOLING USES
ALGAE INHIBITORS AND pH ADJUSTORS ARE USED. EFFECTS: HIGH T (THERMAL POLLUTION), TDS, ACIDITY, ALKALINITY, ETC.
INDUSTRIAL WASTES
NONRECLAIMABLE WASTEWATER
HIGH TDS, TOXICITY
SOLID WASTES
RECLAIMABLE WASTEWATER
LOW TDS, FREE OF TOXICITY
OCEAN OUTFALL
(TOXIC EFFECTS ON MARINE HABITAT)
SANITARY LANDFILL
INJECTION INTO DEEP SALINE AQUIFERS
RECYCLED FOR INDUSTRIAL USE
TO MUNICIPAL WASTEWATER TREATMENT PLANT
PRIMARY, SECONDARY, OR TERTIARY.
DISPOSAL IN STREAMS OR INJECTION INTO AQUIFERS
SLUDGE
REUSE (BACK TO RESOURCE POOL)
RECHARGE OF GROUNDWATER BASINS
SURFACE WATER STREAMS
SANITARY LANDFILL
SLUDGE LAGOONS
OCEAN OUTFALL

Figure 47. Industrial uses of water and their effects on water quality (modified after Hassan, 1974).

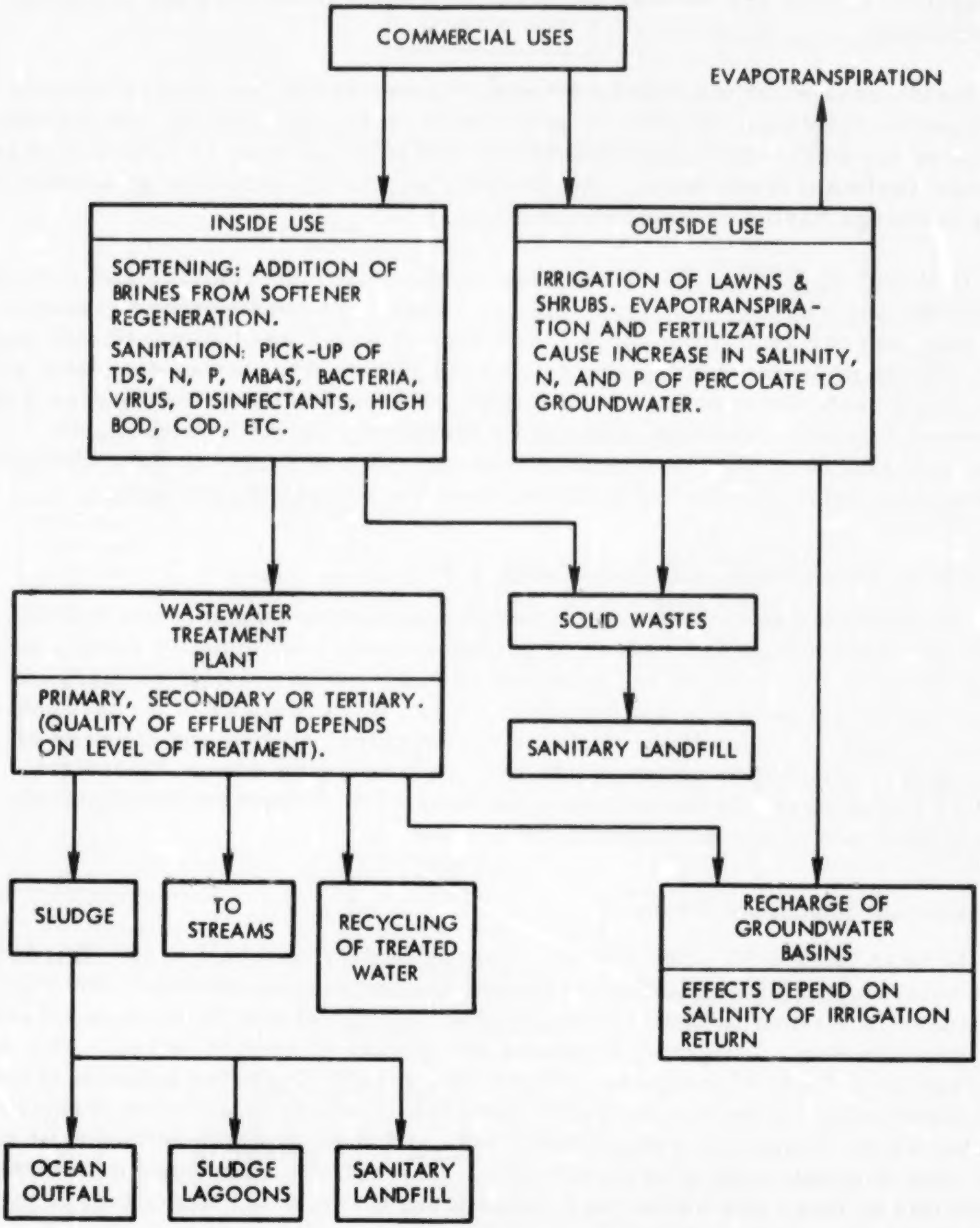
COMMERCIAL USES
EVAPOTRANSPIRATION
INSIDE USE
SOFTENING: ADDITION OF BRINES FROM SOFTENER REGENERATION.
SANITATION: PICK-UP OF TDS, N, P, MBAS, BACTERIA, VIRUS, DISINFECTANTS, HIGH BOD, COD, ETC.
OUTSIDE USE
IRRIGATION OF LAWNS & SHRUBS. EVAPOTRANSPIRATION AND FERTILIZATION CAUSE INCREASE IN SALINITY, N, AND P OF PERCOLATE TO GROUNDWATER.
WASTEWATER TREATMENT PLANT
PRIMARY, SECONDARY OR TERTIARY. (QUALITY OF EFFLUENT DEPENDS ON LEVEL OF TREATMENT).
SOLID WASTES
SANITARY LANDFILL
SLUDGE
TO STREAMS
RECYCLING OF TREATED WATER
RECHARGE OF GROUNDWATER BASINS
EFFECTS DEPEND ON SALINITY OF IRRIGATION RETURN
OCEAN OUTFALL
SLUDGE LAGOONS
SANITARY LANDFILL

Figure 48. Commercial uses of water and their effects on water quality (modified after Hassan, 1974).

Irrigation effects are similar to those previously mentioned for irrigated agriculture.

Inside uses embrace water softening plants, sanitation uses in schools and public buildings, laundries, and commercial laboratories, among others. Most of the waste water generated from commercial uses is disposed of in sewer systems; from there, after treatment, it may return to groundwater via recharge basins or sanitary landfills.

DOMESTIC USES. Domestic uses of water include drinking and cooling, cleaning and bathing, laundry, sanitary needs, air conditioning, garden watering, and for swimming pools. The flow of water used domestically and the effects on water quality are outlined in Figure 49. Inside domestic water uses are basically nonconsumptive uses. Per capita water use varies widely between city and suburban areas and with income levels of households. Water softening may also be a quality consideration of domestic use. Effects of outside water uses are similar to those for irrigated agriculture.

SOURCES AND CAUSES OF POLLUTION

Groundwater pollution results from the activities of man; consequently, the various sources and causes of pollution would conceptually form a long and complex list. However, in terms of basic causes and of primary influences on groundwater quality, the list can be condensed to a reasonable size. Table 11, therefore, contains the principal causes and sources of groundwater pollution grouped into four general categories. Each item listed is discussed in the following sections with respect to its magnitude, locations, and effect on groundwater quality.

Agricultural Sources and Causes

IRRIGATION RETURN FLOW. Approximately one-half to two-thirds of the total water applied during irrigation is used consumptively. The remainder is termed irrigation return flow, which returns to surface streams or groundwater. Irrigation degrades the quality of applied water. The increase in salinity of irrigation return flow results from the addition of salts by dissolution during the irrigation process, from salts added to irrigation water as fertilizers or soil amendments, and from the concentration of salts by evapotranspiration of applied water. The salinity of irrigation return flow due to these processes may range from three to ten times that of the applied water (Jenke, 1974).

The principal cations of return flow are calcium, magnesium, sodium, and potassium. Minor amounts of iron, aluminum, manganese, and other cations may also be present. The dominant anions include carbonate, bicarbonate, sulfate, chloride, and nitrate.

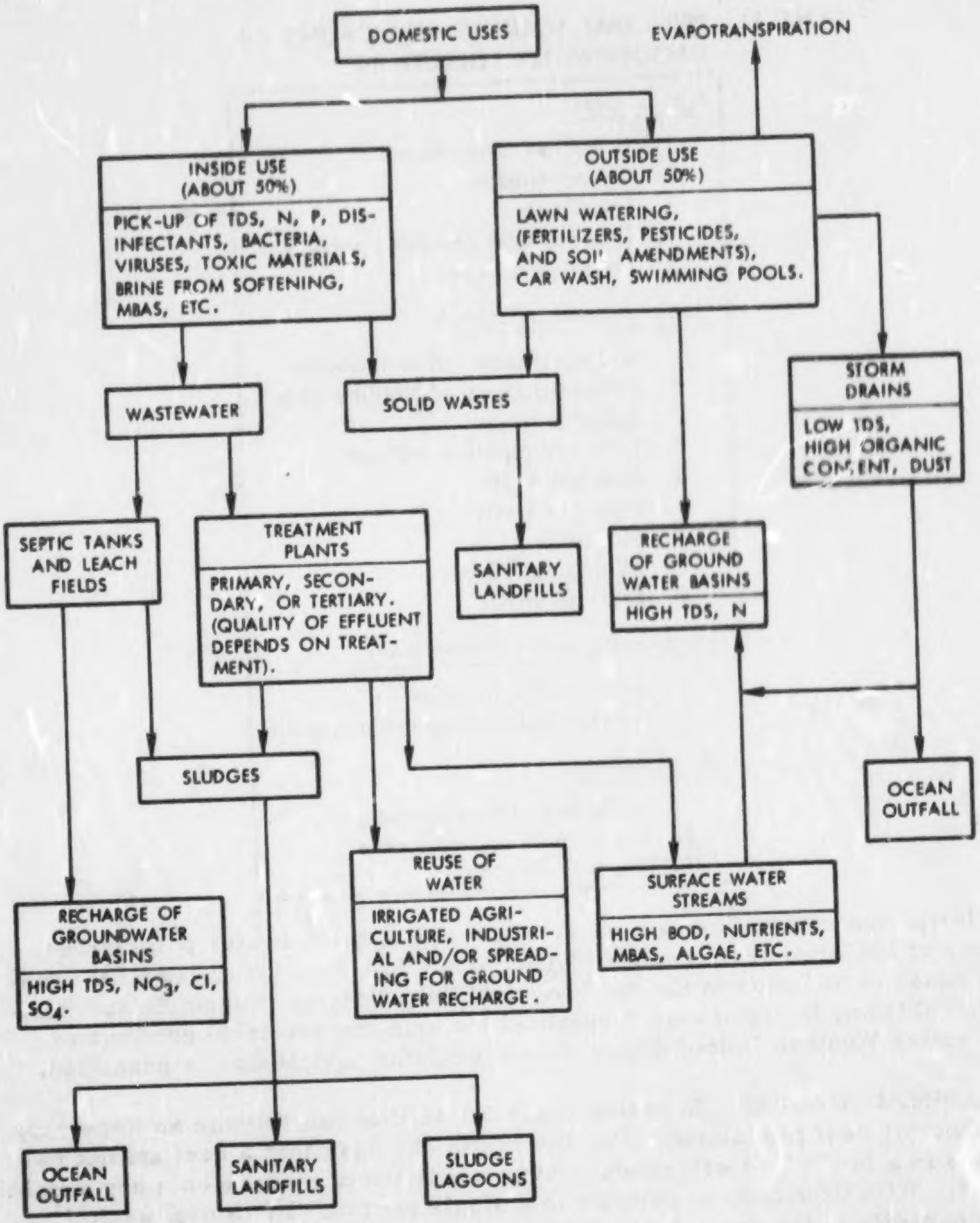
DOMESTIC USES
EVAPOTRANSPIRATION
INSIDE USE (ABOUT 50%)
PICK-UP OF TDS, N, P, DISINFECTANTS, BACTERIA, VIRUSES, TOXIC MATERIALS, BRINE FROM SOFTENING, MBAS, ETC.
OUTSIDE USE (ABOUT 50%)
LAWN WATERING, (FERTILIZERS, PESTICIDES, AND SOIL AMENDMENTS), CAR WASH, SWIMMING POOLS.
WASTEWATER
SOLID WASTES
STORM DRAINS
LOW TDS, HIGH ORGANIC CONTENT, DUST
SEPTIC TANKS AND LEACH FIELDS
TREATMENT PLANTS
PRIMARY, SECONDARY, OR TERTIARY. (QUALITY OF EFFLUENT DEPENDS ON TREATMENT).
SANITARY LANDFILLS
RECHARGE OF GROUND WATER BASINS
HIGH TDS, N
SLUDGES
OCEAN OUTFALL
REUSE OF WATER
IRRIGATED AGRICULTURE, INDUSTRIAL AND/OR SPREADING FOR GROUND WATER RECHARGE.
SURFACE WATER STREAMS
HIGH BOD, NUTRIENTS, MBAS, ALGAE, ETC.
RECHARGE OF GROUNDWATER BASINS
HIGH TDS, NO3, Cl, SO4.
OCEAN OUTFALL
SANITARY LANDFILLS
SLUDGE LAGOONS

Figure 49. Domestic uses of water and their effects on water quality (modified after Hassan, 1974).

TABLE 11. PRINCIPAL SOURCES AND CAUSES OF GROUNDWATER POLLUTION

Agricultural

1. Irrigation return flow
2. Animal wastes
3. Fertilizers
4. Crop residues and dead animals
5. Pesticide residues

Municipal and Industrial

1. Surface disposal of solid wastes
2. Surface disposal of liquid wastes
3. Sewer leakage
4. Tank and pipeline leakage
5. Disposal wells
6. Injection wells
7. Stockpiles
8. Mining activities
9. Oilfield brines

Groundwater Basin Management

1. Saline water intrusion
2. Aquifer interchange through wells

Miscellaneous

1. Spills and surface discharges
2. Septic tanks and cesspools
3. Highway deicing

Irrigation return flow is a nonpoint source of groundwater pollution because of its large areal extent. The problem has been identified as the major cause of pollution in the Southwestern United States (Fuhriman and Barton, 1971) and is significant throughout the arid and semiarid portions of the entire Western United States where irrigated agriculture is practiced.

ANIMAL WASTES. In recent years the feedlot has become an important method for beef production. For the 120 to 150 days that a beef animal remains in a feedlot, it will produce over a half-ton of manure on a dry weight basis. With thousands of animals in a single feedlot, the natural assimilative capacity of the receiving soil is heavily overtaxed. Runoff from rainfall that comes in contact with manure may carry high concentrations of pollutants into ponds, streams, and groundwater.

Animal wastes release salts, organic loads, and bacteria into the soil. Investigations have shown that nitrate-nitrogen is the most important persistent pollutant that reaches the water table (Fuhriman and Barton, 1971). Where permeability is moderate and the depth to water table is large, most biological feedlot pollutants are removed in the vadose zone before reaching the groundwater.

Feedlot operations are largest in Texas and California; however, they can be found throughout the western and central portions of the United States.

FERTILIZERS. The application of fertilizers to agricultural land usually results in a portion of the fertilizer being leached through the soil and into the underlying groundwater. The most important constituents are compounds of nitrate and phosphorus. Most phosphate fertilizers, however, are readily adsorbed on soil particles so that they seldom constitute a groundwater problem. But nitrogen in solution is only partially used by plants and also may be adsorbed to only a limited extent by the soil or lost in gaseous form to the atmosphere; consequently, nitrogen has been found to be the primary fertilizer element related to groundwater pollution (Fuhriman and Barton, 1971).

The use of fertilizers is extensive in the United States and will increase in the future. Therefore, fertilizer usage leading to the potential for nitrogen pollution of groundwater on a nonpoint source basis can be expected to continue. Furthermore, high nitrate concentrations observed in groundwaters of suburban areas suggest the possibility of lawn fertilizers as a source (Miller, 1974).

CROP RESIDUES AND DEAD ANIMALS. Crop residues are those portions of a plant left in the field or processing shed after harvest. For every pound of food marketed, from 2 to 5 pounds of residues are left in the field or in the packing shed (Fuhriman and Barton, 1971). Although such wastes can create groundwater pollution problems, there is little evidence available to show that they do.

Larger farm animals, when dead, are usually disposed of by rendering plants, and seldom affect groundwater quality. Similarly, dead sheep or wildlife on the range are usually quickly disposed of by other forms of wildlife. Bodies of animals used in laboratory experiments, particularly those subjected to radioactive treatments, must be disposed of with special care.

The disposal of dead poultry is probably the only source which can create a serious groundwater pollution hazard. Poultry producers today often handle flocks exceeding 100,000 fowl. The death rate in such an operation can average 35 fowl per day (Fuhriman and Barton, 1971). Many producers dispose of dead birds by burial in a large trench; consequently, with percolating water in the vicinity of such a mass of decaying organic matter, the groundwater pollution potential is considerable.

PESTICIDE RESIDUES. The term "pesticide" is here broadly interpreted to embrace any material used to control, destroy, or mitigate pests, including insecticides, herbicides, fungicides, nematocides, rodenticides, bactericides, growth regulators, and defoliants. Whenever these materials occur in groundwater, even in minute concentrations, the consequences are serious in terms of the potability of the water.

The magnitude of the threat of pesticides to groundwater quality depends upon the properties of the pesticide residue; the frequency and rate of rainfall or irrigation; the hydrologic characteristics of the soil; and the volume, the state (liquid or solid), and the persistence of the pesticide applied (Todd and McNulty, 1974). Many pesticides are relatively insoluble in water; many also are readily adsorbed on soil particles.

Municipal and Industrial Sources and Causes

SURFACE DISPOSAL OF SOLID WASTES. The land disposal of solid wastes constitutes an important source of groundwater pollution. A landfill may be defined as any land area used for the deposit of urban, or municipal, solid waste. Estimates of the production of solid wastes indicate a total of about 1 ton per capita per year, equal to almost 6 pounds per person per day (Meyer, 1973). Because wastes are generated and disposed of where people are living, the pattern of urban population distribution gives an indication of the location and intensity of landfill practice.

There are two basic types of landfills: one is the sanitary landfill, designed and constructed according to engineering specifications, while the other is simply a refuse dump. Of the more than 100,000 landfills in the United States, probably no more than 10 percent can be classed as sanitary landfills.

Leachate from a landfill can pollute groundwater. For this to occur, however, a source of water moving through the fill material is required. Possible sources include precipitation, moisture content of refuse, surface water infiltrating into the fill, percolating water entering the fill from adjacent land, or groundwater in contact with the fill (Meyer, 1973). Leachate is not produced in a landfill until a significant portion of the material has a moisture content equal to field capacity. Ordinary mixed refuse contains a high paper content and usually has a moisture content far below that of field capacity.

It follows, therefore, from the above reasoning that leachate from a landfill can be prevented if refuse can be compacted and covered without becoming saturated, if rainfall and surface runoff can be diverted from the landfill material, and if the fill material can be isolated from nearby groundwater. These are esentially the goals of a well-designed sanitary landfill. With a properly constructed landfill, any leachate generated can be controlled and prevented from polluting groundwater. Accomplishment of these objectives is possible by proper site selection, by placement of appropriate cover material, and by surface and subsurface leachate collection systems. The problem of pollution from landfills is greatest in the Eastern United States where high rainfalls and shallow water tables occur. Conversely, the problem is minimal in portions of the arid Southwest where deep water tables are found.

Analyses of leachate show that its quality can vary widely. The most important pollutants are COD, BOD, iron, chloride, and nitrate. In addition, hardness, alkalinity, and total dissolved solids are often increased. Gases, including methane, carbon dioxide, ammonia, and hydrogen sulfide, are a further byproduct of landfills; these may cause subsurface chemical reactions which can degrade groundwater quality.

SURFACE DISPOSAL OF LIQUID WASTES. There are few, if any, industries which do not make use of water, either directly as part of the product, such as in beverage industries and in steam generation, or indirectly as for cooling water and as a transporting medium (paper industry). Water is often used as a solvent either as a medium for chemical reactions or for washing products and containers, or machines, apparatus, factory floors, etc. Much of the water is subsequently discharged as waste water, the composition of which differs according to the usage and nature of the process used.

Wastes from a particular type of industry are usually similar enough from factory to factory to be compared directly. The waste composition and volumes are often correlated with production rates. Industrial wastes may be broadly classified as:

- Nonfermentable inorganics and other inert wastes
- Fermentable, mainly organic wastes
- Toxic wastes.

Waste pickling-bath solutions from sheet-metal or galvanizing shops are examples of nonfermentable wastes, however they may also be toxic due to low pH and the presence of trace elements. Many food industries discharge readily fermentable wastes; for example, meat-packing plants and canneries. However, these wastes may also be toxic due to low pH from sulphurous acid, or because of plating shop wastes which are discharged along with packing shop wastes. Industries which commonly discharge toxic wastes include dyehouses and electroplaters (cyanides, sulfides, chromium, or copper) and chemical factories manufacturing chlorinated hydrocarbons, etc. Dyehouse wastes are usually mineralized and may also contain significant amounts of fermentable organic matter. Waste waters from the use of water for cooling purposes may be relatively unpolluted, except for temperature (Imhoff et al., 1971).

Several major types of industrial waste of importance to groundwater pollution are cooling water, process wastes, boiler blowdown, washdown water, storm runoff, stockpiles, water treatment plant effluent, tank and pipeline leakage, and hydrocarbon storage. These wastes are disposed of by a variety of methods and often in combination.

Cooling Water. Cooling water comprises the greatest industrial use of water. Cooling water is often disposed of in percolation ponds and disposal wells, and is sometimes used for irrigation.

Process Wastes. Process wastes probably present the most serious threat to groundwater quality of all types of industrial wastes. These wastes include spent fluids, catalysts, byproducts, and other wastes. These wastes are commonly disposed of in wells and percolation ponds.

Boiler Blowdown. Boiler blowdown is one of the common types of industrial wastes, and may commonly be combined with other types of wastes before disposal.

Washdown Water. Water for floor washing is often highly polluted from acids, solid wastes, and other substances. This waste is also commonly combined with other types of waste prior to disposal.

Storm Runoff. Precipitation on uncovered surfaces at industrial sites may pick up significant levels of pollutants. This water may be gathered and disposed of in a percolation pond, dry stream bed, disposal well, or used for irrigation. The quality largely depends on housekeeping procedures of the industry and the type of material that may be spilled or leaked at the land surface.

Stockpiles. The piling of solid raw materials, products, byproducts, and waste materials on the ground without protection from precipitation can cause groundwater pollution.

Water Treatment Plant Effluent. Varying amounts of treatment may be required for various industries depending on the quality of source water. Water treatment commonly involves filtration and clarification, water softening, and demineralization or deionization. Disposal is commonly by percolation ponds or disposal wells. This waste may present a substantial pollutant load in the case of waste brines.

Tank and Pipeline Leakage. One of the sources of groundwater pollution currently receiving considerable attention is small leaks in tanks and pipelines.

Hydrocarbon Storage. Facilities for hydrocarbon storage or disposal are often constructed so as to permit inadvertent groundwater pollution.

The disposal of municipal and industrial liquid wastes on the ground surface involves not only a wide range of potential groundwater pollutants but also several methods of release of effluents. The topic can be discussed under three basic techniques of disposal — into land depressions, by spraying, and into stream beds.

Natural or artificial depressions in the ground surface for waste disposal are usually referred to as lagoons, basins, or pits. These may be lined or unlined, but in either case, leakage to groundwater is a possibility. These structures are intended to serve any of a variety of purposes; to name a few, storage, processing, waste treatment, cooling, evaporation, and disposal. It is now widely recognized that many so-called "evaporation" ponds are in reality essentially percolation ponds. The once common practice of discharging oilfield brines into open pits is now largely past as a result of State regulatory practices; however, the effects on groundwater quality remain in many localities.

The type of pollution created clearly depends upon the type of waste material, its volume and concentration, the soil and aquifer conditions, and the location of groundwater. Sewage disposal into a lagoon usually results in the removal of bacteria and suspended organic matter after only a few feet of movement underground; however, dissolved organic matter can persist for longer distances. Removal of pollutants may be minimal for percolation through cavernous or highly fractured rocks. The increase in mineral content of groundwater can be considerable, as shown by Table 12. Urban runoff collected in storm sewers can contribute BOD, COD, nitrate, lead, gasoline, oil, and grease, among other pollutants.

TABLE 12. NORMAL RANGE OF MINERAL PICKUP IN DOMESTIC SEWAGE (Todd, 1970)

Mineral Constituents	Normal Range in mg/l (except as noted)
Total Dissolved Solids	100-300
Boron	0.1-0.4
Percent Sodium	5-15%
Sodium	40-70
Potassium	7-15
Magnesium	15-40
Calcium	15-40
Total Nitrogen	20-40
Phosphate	20-40
Sulfate	15-30
Chloride	20-50
Total Alkalinity	100-150

Effluents percolating from industrial lagoons or basins have a greater potential to degrade groundwater from a constituent standpoint than does domestic sewage effluent, but not volumetrically. These industrial liquids may contain brines, arsenic compounds, heavy metals, acids, petroleum products, phenols, radioactive substances, as well as other miscellaneous chemicals (Todd and McNulty, 1974; Meyer, 1973). And some of these materials are capable of traveling long distances in groundwater.

Spray irrigation has become a common practice for disposal of waste water by fruit and vegetable processors and of treated sewage by municipalities. Studies of the effect of spray effluents on groundwater have indicated that vegetation often takes up a substantial fraction of the nitrogen as compared to percolation beneath a bare soil. Thus, the adverse effect on groundwater quality may be limited to an increase in total dissolved solids. Compared to lagoons, however, spray irrigation differs in that it provides a greater opportunity for waste water to contaminate surface runoff during rainfall periods (Meyer, 1973).

Because spraying is basically a method of waste water disposal, nutrient removal, and water reclamation, it can be expected to increase in the future. The practice should be limited to predominantly organic wastes that can be readily assimilated in the soil zone so that any effect on quality of groundwater is minimized.

Disposal of partly treated sewage and industrial wastes into the beds of intermittent and ephemeral streams is practiced mainly in the arid and semi-arid regions of the Southwestern United States (Meyer, 1973). Stormwater runoff is also similarly discharged in many parts of the country. The benefit of these procedures is the replenishment of groundwater resources.

Pollutants that enter an aquifer beneath a stream bed depend on the character of the wastes, the type of stream-bed material, the depth to the water table, and the type of treatment given to the wastes. For domestic wastes the potential pollutants include chloride, organic compounds, nitrogen compounds, phosphates, boron, synthetic detergents, bacteria, viruses, and perhaps pesticides. For industrial wastes, the spectrum of possible pollutants becomes much broader; in general, those of greatest concern include heavy metals and organics such as phenols and polychlorinated biphenyls.

SEWER LEAKAGE. Conceptually, a sanitary sewer is intended to be watertight and thus to present no hazard to groundwater quality. In reality, however, leakage, especially from old sewers, is a common occurrence. Leakage from gravity sewers may result from poor workmanship, defective sewer pipe sections, breakage by tree roots or other causes, ruptures from heavy loads, rupture by soil slippage, fractures by seismic activity, loss of foundation support due to washouts, shearing due to differential settlement at manholes, and infiltration causing sewage to flow into abandoned sewer laterals (Meyer, 1973).

Sewer leakage releases raw sewage into the ground, often close to groundwater. This can introduce high concentrations of BOD, COD, chlorides, unstable organics, and bacteria into groundwater. On the other hand suspended solids tend to clog sewer cracks, and the surrounding soils tend to become clogged due to anaerobic conditions; therefore, the actual effect of sewer leakage may be less than the theoretical potential.

TANK AND PIPELINE LEAKAGE. Underground storage and transmission of a wide variety of fuels and chemicals is a common practice for commercial, industrial, and individual uses. These tanks and pipelines are subject to structural failures from several causes, and the subsequent leakage becomes a source of groundwater pollution.

Petroleum and petroleum products, because of their large usage, are responsible for most of the pollution. Thus, 90 percent of the interstate liquid pipeline accidents reported in 1971 involved crude oil, gasoline, liquefied propane gas, or fuel oil (Meyer, 1973). Major causes of these pipeline leaks were corrosion, equipment rupturing the pipelines, defective pipe seams, or incorrect operations by handling personnel.

Leakage is particularly frequent from small installations such as home fuel oil tanks and gasoline stations, where installation, inspection, and maintenance standards may be low. In Maryland some 60 instances of groundwater pollution were reported in a single year from gasoline stations; and in northern Europe, where most homes are heated by oil stored in subsurface tanks, oil pollution has become the major threat to groundwater quality (Meyer, 1973).

Liquid radioactive wastes are sometimes stored in underground tanks. Leakage has been reported from an installation at Hanford, Washington.

Leakage of an immiscible liquid such as oil into the ground will cause the oil to move downward in relatively permeable soils or, if the leak is from a pipeline in relatively impermeable soil, the oil will tend to remain in the trench and move in the down-slope direction. Oil coats soil particles as it advances; therefore, if the quantity of leaked liquid is sufficiently small, the total flow may become immobilized. Subsequent infiltrating water will tend to transport the pollutant from the soil particles downward to the water table. Once oil reaches a water table it spreads to form a thin layer on top of the water table and then to migrate laterally with the groundwater body.

DISPOSAL WELLS. Many thousands of wells throughout the United States are used for disposal of pollutants into freshwater aquifers. Examples include electronic industries disposing of metal-plating wastes in

Arizona; domestic sewage disposal from individual homes in Florida and Texas; low-level radioactive wastes at one location in Idaho; and heated water from cooling systems in New York, California, and several midwestern States (Meyer, 1973).

In recent years considerable attention has been given to the possibility of injecting treated municipal sewage into wells penetrating freshwater aquifers. Several of the proposed schemes not only would solve a sewage-disposal problem but also would help to recharge freshwater aquifers or to establish hydraulic barriers against saltwater encroachment in freshwater aquifers. Advanced pilot plant experiments are being conducted in Long Island and in California (Meyer, 1973). Sewage must be given at least secondary treatment and preferably tertiary treatment to prevent clogging of the disposal wells and to reduce or prevent significant chemical and bacteriological pollution of the aquifer.

Modification of the quality of groundwater caused by subsurface disposal of wastes through wells depends on a variety of factors, including the composition of the native water, the amount and composition of the injected waste fluid, the rate of injection, the permeability of the aquifer, the type of well construction, and the kinds of biological and chemical degradation that may occur. Most wells used for disposal of polluted liquids are, for economic reasons, located in the shallowest available aquifer.

INJECTION WELLS. Deep injection wells are employed for disposal of industrial wastes and oilfield brines. At present there are fewer than 300 industrial disposal wells in the United States (Meyer, 1973), but there are more than 70,000 brine disposal wells.

It has been common practice in the past to use abandoned oil production wells for brine disposal. Because the wells were not designed, cased, or cemented for brine injection, there have been numerous instances of injection wells with undetected ruptures beneath the surface where injected brines have seeped into freshwater aquifers for many years before being discovered. Some State regulatory agencies have alleviated this problem by requiring an injection tubing inside a casing. The space between the tubing and casing is filled with a fluid which is monitored to detect ruptures.

Currently, most oilfield brines are returned to subsurface formations either for secondary recovery in an oil-producing formation or just as a disposal method. However, even with properly designed and constructed injection wells, brine disposal presents pollution problems because of the numerous oil, gas, injection, and test holes, which for many years were simply abandoned without proper plugging. Unplugged wells provide vertical pathways for injected brines to rise into overlying freshwater aquifers.

Because of the limited number of industrial waste injection wells and the careful attention given to their siting, design, and operation by State regulatory agencies, there have been few reported cases of groundwater pollution from this source; however, the potential for this to occur at distances from such wells should not be minimized.

STOCKPILES. Stockpiles of solid materials are a commonly found sight around industrial plants and at construction sites. These may be raw materials awaiting use, or they may be solid wastes placed for temporary or permanent storage. Precipitation falling on unsheltered stockpiles causes leaching to occur which may then transport heavy metals, salt, and other inorganic and organic constituents as pollutants to the groundwater. Only by storing solid wastes in bins or shelters can this source of groundwater pollution be effectively controlled.

MINING ACTIVITIES. A variety of groundwater pollution problems can be associated with mining activities. Mines fall into two basic categories — surface mines and underground mines. Pollution effects depend on the material being extracted and the milling process; coal mines are a major contributor; metallic ores for production of iron, copper, zinc, and lead are of secondary importance; while stone, sand, and gravel quarries are numerous but chemically much less important.

Both surface and underground mines invariably extend below the water table so that dewatering to further mining activity is common. The water so pumped, either directly from the mine or from nearby wells, may be highly mineralized and is frequently referred to as "acid mine waters." Although there is no typical analysis of mine drainage water, normal characteristics include low pH, high acidity, high ferrous or ferric iron, high aluminum, and high sulfates (Miller, 1974). The magnitudes of the various constituents vary with the extent of oxidation and/or neutralization of the drainage water.

Many economic deposits of coal and other minerals found in bedrock are associated with sulfide minerals, pyrite (FeS_2) being one of the most prominent. Pyrite and most other sulfides are stable under the conditions that exist below the water table. However, if the water table is lowered, oxidation of the sulfides occurs in the dewatered zone. Oxidation of pyrite followed by contact with water produces ferrous sulfate ($FeSO_4$) and sulfuric acid (H_2SO_4) in solution. This situation may arise where a mine is abandoned and dewatering activities cease or by downward percolating rainwater. The net result is that this solution is introduced into the groundwater system, causing a drop in pH, and a rise in sulfate and iron content (Miller, 1974).

In the mining and milling of ores groundwater pollution can result from a variety of processes. With copper ore, for example, reagents are added during milling; these include lime, arsenic, cyanide, kerosene, and organic materials. The crushing of sulfide-related ores can release copper sulfate, molybdenum, potassium, and high total dissolved solids. The leaching of ores in oxide form with acids can contribute iron, manganese, low pH, copper, molybdenum, and high total dissolved solids. The use of explosives in fracturing overburden or ore has potential to introduce ammonium nitrate to groundwater.

Pollution of groundwater can also result from the leaching of old mine tailings and from settling ponds. Uranium mill tailings are radioactive so that this could become a source of localized pollution. Serious pollution problems can be associated with both active and abandoned mines.

OILFIELD BRINES. The production of oil and gas is usually accompanied with the production of waste water in the form of brines. The ratio of brine to oil or gas varies with location and with the age of a well. A recent study in the Southcentral States (Scalf et al., 1973) reported about three barrels of brine were produced for each barrel of oil. The chief constituents of brine typically include sodium, calcium, ammonia, boron, chloride, sulfate, trace metals, and of course, high total dissolved solids.

Until recently the common methods of oilfield brine disposal consisted of discharge to streams or to "evaporation" ponds. In both cases brine-polluted aquifers became commonplace in oil production areas as infiltrating water from streams and ponds moved to the groundwater. Thousands of unlined brine pits were in use in the Southcentral States until only a few years ago when they were prohibited by the oil regulatory agencies of the various States. Despite this ban and the fact that few of the brine-affected areas have been mapped, enough have been located to indicate a serious groundwater pollution problem for many years to come (Todd and McNulty, 1974; Scalf et al., 1973). Because of the slow movement of groundwater, brine-polluted groundwater is only now being discovered in many areas of oil development abandoned 20 or 30 years ago.

With the ban on unlined evaporation pits, oil companies were forced to construct pits lined with impervious material or to inject brines back into the oil-bearing formation or into another formation sufficiently removed from freshwater aquifers to prevent contamination (see previous subsection on Injection Wells). Nevertheless, there are numerous reported and suspected violations of these regulations, primarily in the form of bypassing brine pits, by accidental or deliberate rupture of pit liners, by overflowing waste pits, or by leakage from broken lines.

In oil-producing areas brines represent one of the major causes of groundwater pollution. Case studies of the problem have been extensively documented (Todd and McNulty, 1974; Scalf et al., 1973).

SALINE WATER INTRUSION. Saltwater may invade freshwater aquifers to create point or nonpoint sources of pollution. In coastal aquifers seawater is the pollutant; in inland aquifers any of several sources of saline water may be responsible.

Under natural conditions fresh groundwater in coastal aquifers is discharged into the ocean. If, however, localized pumpage becomes sufficiently large, the seaward flow is decreased or even reversed, thereby causing seawater to advance inland within the aquifer. Almost all of the coastal States of the United States have some coastal aquifers polluted by the intrusion of seawater (Meyer, 1973). Florida is the most seriously affected State, followed by California, Texas, New York, and Hawaii.

The usual cause of seawater intrusion in coastal aquifers is overpumping. In flat coastal areas, drainage channels or canals can also cause intrusion. They can contribute to the problem in two ways — one by reducing the water table elevation and its associated freshwater flow, and the other by permitting seawater during periods of high tide to advance long distances inland where it can infiltrate into the ground. On oceanic islands freshwater from rainfall percolates to form a lens overlying seawater. If a well penetrating the lens is pumped at too high a rate, the underlying seawater will rise and pollute the water supply of the well.

At the boundary between freshwater and seawater underground, dispersion and diffusion, together with external influences such as recharge from precipitation, pumping of wells, and tidal action, combine to create a transition zone of brackish water. Figure 50 shows a vertical cross-section of a coastal aquifer together with the transition zone and associated circulations.

In inland aquifers saline water can be found at increasing depths from seawater which entered aquifers during deposition or during a high stand of the sea in geologic time. Approximately two-thirds of the United States is underlain in part by saline groundwater, often referred to as connate water. In addition, localized saline zones may occur from unique geologic formations or topographic features or from saline wastes contributed by man.

The most common mechanism of intrusion is that caused by overpumping of a well which causes an upconing of underlying saline water toward the well. This upward movement is illustrated in Figure 51. Where freshwater and saline aquifers are connected, a lowering of the water table can induce an upward movement of saline water. Thus, dewatering operations, as for quarries, roads, or excavations, or the dredging of a stream channel can contribute to the encroachment of saline water into aquifers.

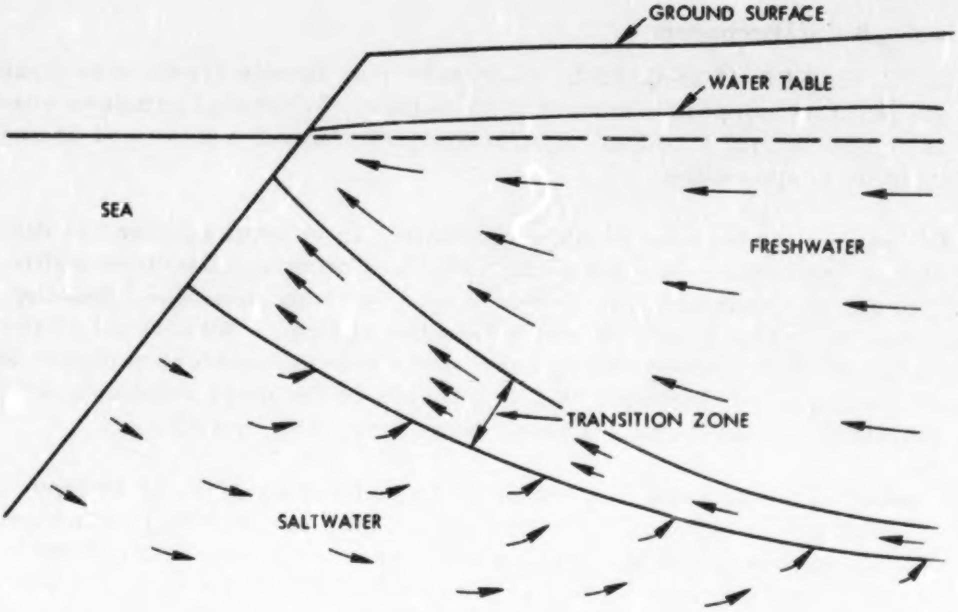

Figure 50. Schematic vertical cross section through a coastal aquifer showing freshwater and seawater circulations with a transition zone (Meyer, 1973).

AQUIFER INTERCHANGE THROUGH WELLS. Because wells form highly permeable vertical connections between aquifers, they can serve as important means for groundwater pollution. This usually happens, however, only where attention is not given to the proper construction, sealing, or abandonment of wells.

Pollution occurs where well screens, perforated casing, or an open borehole interconnects two separate aquifers, or where the surface casing has not been adequately sealed. In these instances water wells can serve as mechanisms for transmission of pollutants from one aquifer to another or from land surface to an aquifer. Interaquifer exchange occurs where there are vertical differences in hydraulic head between aquifers.

A common problem of this type is the vertical movement of saline water into a freshwater aquifer. Abandoned and corroded well casings allow the saline water to enter either from an overlying or underlying saline water aquifer or from an adjacent saline surface water body. The problem is well illustrated by situations in Baltimore, Maryland, (Miller, 1974) and Alameda County, California, (Meyer, 1973).

If a well is improperly sealed in the annular space between the casing and the borehole and connects aquifers of different water quality, polluted water can move along the exterior of the well casing and enter the well.

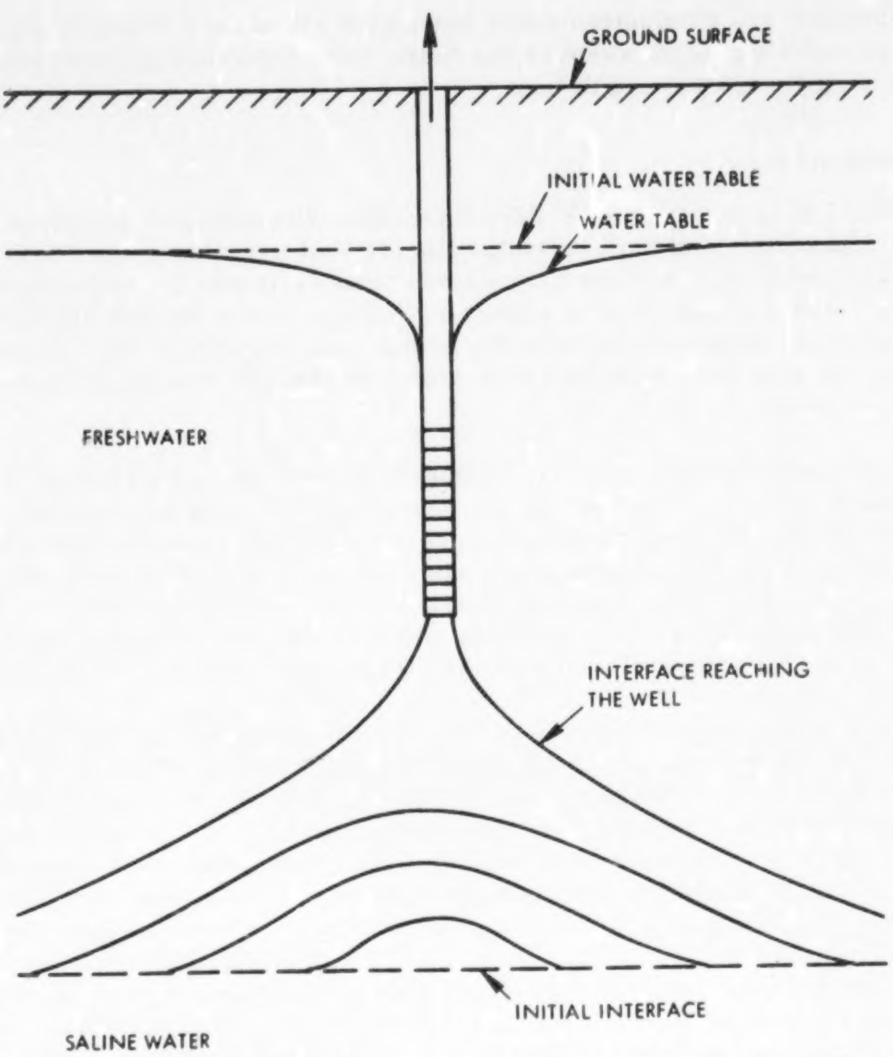
GROUND SURFACE
INITIAL WATER TABLE
WATER TABLE
FRESHWATER
INTERFACE REACHING THE WELL
INITIAL INTERFACE
SALINE WATER

Figure 51. Schematic diagram of upconing of underlying saline water to a pumping well.

In addition, if provisions are not made to divert surface water away from a well, it can drain downward into a well. Most public water supply wells are properly sealed, inspected, and maintained, but surveys by health authorities have revealed that private wells serving individual residences often are not protected against pollution from overland runoff containing septic fluids, barnyard wastes, or storm waters.

In most States today, regulations exist requiring plugging of abandoned wells. But there are many thousands of abandoned wells which remain unplugged either because they cannot be located or because changes in property ownership with time make the responsibility for plugging indeterminate. The problem is particularly serious in oil and gas areas where numerous exploration and production wells have been abandoned (Scalf et al., 1973). These holes serve as avenues for brine from injection wells to rise into overlying freshwater aquifers.

Miscellaneous

SPILLS AND SURFACE DISCHARGES. Groundwater pollution can result from hazardous and nonhazardous liquids that are discharged onto the ground surface in an uncontrolled manner and then seep into the underlying soils. If the volume of the fluid is sufficiently large, the pollutant can migrate down to the water table and degrade the groundwater quality. Any of a variety of activities can lead to spills and surface discharges that may serve as pollution sources.

Poor housekeeping at large industrial plants and airports is a contributory pollution cause. At industrial sites, causal activities may include boilovers and blowoffs, overpumping during transfer of liquids to or from storage and carriers, leaks from faulty pipes and valves in product distribution systems, and poor control over waste discharges and storm-water runoff. At airports the washing of planes with solvents and spills of fuel can form an extensive body of hydrocarbons floating on the water table (Miller, 1974).

Pollution of groundwater also occurs from the intermittent dumping of fluids on the ground, especially at gasoline stations and other types of small commercial establishments. Automotive waste oil is disposed of on the ground by car owners, by commercial garages and gasoline stations, and at construction sites; the total of these many small contributions runs to millions of gallons of oil annually (Miller, 1974). Small industries often dispose of lubricating, hydraulic, and cutting oils by local dumping. It is not uncommon to find small commercial facilities discharging liquid wastes onto undeveloped land, the reasoning being that it is uneconomic to store and to haul the wastes to municipal treatment plants or landfills and that the liquids may be harmful to local septic tanks or cesspools.

Finally, accidents involving aboveground pipes and tanks, railroad cars, and trucks can cause the release of large quantities of a pollutant at a particular site. The use of water to flush spilled fluids, as from a highway, may actually aid in transporting the pollutant down to the water table.

SEPTIC TANKS AND CESSPOOLS. Of all the sources and causes of groundwater pollution, the most numerous and widely distributed is that of septic tanks and cesspools. It is estimated that approximately 40 million persons, or nearly 20 percent of the total population, are served by individual household waste water treatment systems. This means that some 2.5 billion gallons of partially treated sewage is discharged from residences directly into the underground every day. In addition, stores, laundries, small office buildings, hospitals, and industries employ septic tanks in areas where community sewer systems are not available. Furthermore, innumerable summer cabins, Forest Service campgrounds, and organized group camps depend upon subsurface disposal of waste water, primarily during the summer season.

The heaviest concentrations of septic systems are to be found in the suburban subdivisions that developed on the fringes of major cities after World War II. A septic tank is a watertight basin intended to separate floating and settleable solids from the liquid fraction of domestic sewage and to discharge this liquid together with its burden of dissolved and particulate solids into the biologically active zone of the soil mantle through a subsurface percolation system such as a tile field, a seepage bed, or an earth-covered sand filter (Meyer, 1973). A cesspool is a large buried chamber which is walled with a porous material, such as concrete blocks, and designed to receive raw sewage. Although new installations of this latter kind are no longer approved, many thousands of cesspools remain in operation in the United States today wherever soil conditions are favorable.

Domestic sewage adds minerals to groundwater, as indicated in Table 12. Bacteria and viruses are normally removed by the soil system. Phosphorus is generally retained by the soil, but significant quantities of nitrogen can, depending upon local soil and vegetation conditions, be added to groundwater. The degree of groundwater pollution has been shown to be related to the density of septic tank installations (Miller, 1974) and to the local hydrogeologic framework.

HIGHWAY DEICING. A recent and unique problem that has attracted considerable attention is the pollution of groundwater resulting from application of deicing salts to streets and highways in winter. The region most largely affected includes the Northeastern and Northcentral States. The salt reaches the groundwater both from surface stockpiles and from solution of salt that has been spread on roadways.

Salt application quantities by State highway departments of the Northeastern States range from 3 to 20 tons per single-lane mile during a single winter season (Miller, 1974). More than 95 percent of this is sodium chloride, the remainder being calcium chloride. Furthermore, the demand to maintain highways and roads for vehicular use in winter has caused a steady growth in the use of salt for deicing. Data from the State of Massachusetts shows that applied salts increased 700 percent in the 15-year period from 1955 to 1970.

Widespread and long-term degradation of groundwater quality has been the experience with highway deicing salts (Meyer, 1973). In addition, casings and screens of wells have been corroded, necessitating replacement of many wells. The gradual increase in salts has led to some town groundwater supplies exceeding salt limits for persons on low-sodium diets (Todd and McNulty, 1974). Salt concentrations have been found to be highest in areas where salting has been practiced longest, in wells closest to roadways, and during April, the month of greatest snow melt.

QUALITY IN RELATION TO WATER USE

Water Quality Standards

The quality of groundwater is most commonly evaluated relative to its existing or potential use. Because water quality criteria vary with the type of use, a groundwater may be satisfactory for one use but not for another. Thus, pollution, which is the manmade degradation of water quality, may or may not restrict a given groundwater for a particular use. On the other hand increasing pollution leads to increasing impairment for use of water.

The concept of water quality criteria, or standards, can be illustrated by reference to the diagram in Figure 52. Here pollution is related to impairment for use. Up to a threshold level of pollution, water is satisfactory for a given use (such as irrigation, drinking, etc.). This level then defines a water quality criteria or standard. With increasing pollution above this

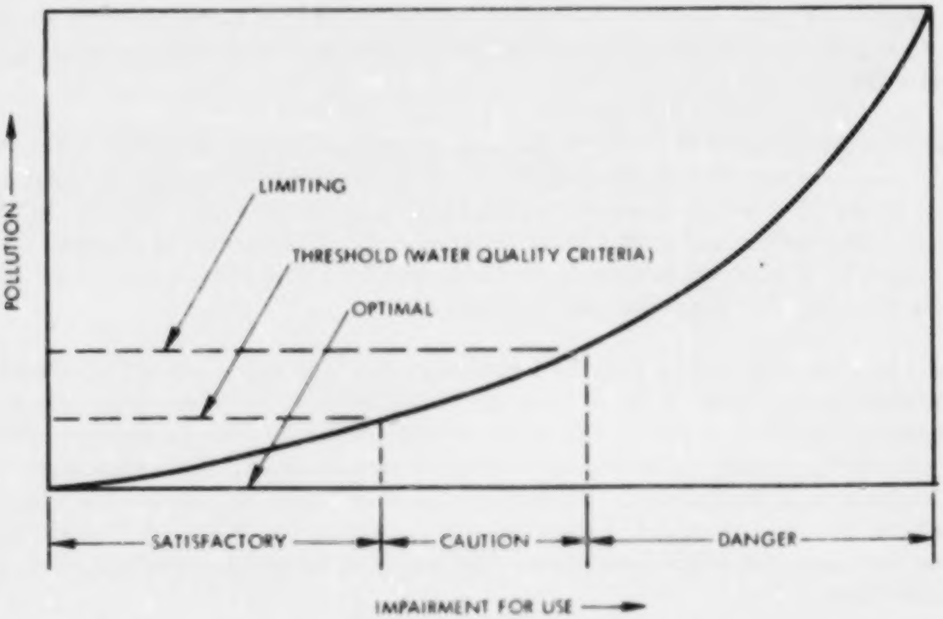

Figure 52. Diagram illustrating the relation of water pollution to impairment for a given water use (modified after McGauhey, 1968a).

level, a relatively narrow cautionary band can be defined. But this terminates at the limiting level of pollution, beyond which increases in pollution constitute a danger for that particular use. Another way of stating this relationship is that pollution up to the threshold level may be regarded as a reasonable impairment, whereas pollution beyond the limiting level becomes an unreasonable impairment. A pollutant may here be defined as any chemical constituent, any biological organism, or any physical characteristic which can adversely affect the use of the water.

Standards or guidelines have been established for all types of water use. Those applicable to the major uses of groundwater are briefly described in the following subsections.

Drinking Water

The most important use of groundwater is for drinking water purposes. Drinking water standards have in the past been set by the U.S. Public Health Service in the United States, and most States have adhered closely to these requirements. The standards are summarized in Table 13. These criteria are under continual review so that new constituents and revised levels of constituents are to be expected with time.

Industrial Water

Quality requirements of waters used in different industrial processes vary widely. For example, makeup water for boilers must meet exacting criteria, whereas water of the quality of seawater can be employed for many cooling purposes. Recommended water quality tolerances for certain industrial applications have been prepared (Todd, 1970) as guidelines.

For industrial purposes the relative constancy of various constituents is as important as the quality itself. A relatively poor quality water can be treated so as to be suitable for a given process, but if the quality fluctuates widely, continual problems and added costs may be involved. From this standpoint groundwater sources are preferred to surface water sources because variations in chemical and physical quality are normally much smaller.

Irrigation Water

The suitability of a groundwater for irrigation depends upon the effects of chemical constituents in the water on the plant and the soil (Todd, 1959). Salts can restrict plant growth physically by modifying osmotic processes and chemically by causing undesirable metabolic reactions. Salts can produce changes in soil structure, permeability, and aeration.

Specific limits of permissible salt concentrations for irrigation water cannot be stated because of variations in salinity tolerance among different plants, as well as in soil type, climatic conditions, and irrigation practices.

TABLE 13. DRINKING WATER STANDARDS OF THE U.S. PUBLIC HEALTH SERVICE (McGauhey, 1968b)

PHYSICAL STANDARDS

	Units
Turbidity	5
Color	15
Threshold Odor Number	3

CHEMICAL STANDARDS

Substance	Recommended Limits of Concentrations, in mg/l	Mandatory Limits of Concentrations, in mg/l
Alkyl Benzene Sulfonate (ABS)	0.5	---
Arsenic (As)	0.01	0.05
Barium (Ba)	---	1.0
Cadmium (Cd)	---	0.01
Carbon Chloroform Extract (CCE)	0.2	---
Chloride (Cl)	250	---
Chromium (hexavalent) (Cr^{+6})	---	0.05
Copper (Cu)	1.0	---
Cyanide (CN)	0.01	0.2
Fluoride (F)	1.7†	2.2†
Iron (Fe)	0.3	---
Lead (Pb)	---	0.05
Manganese (Mn)	0.05	---
Nitrate (NO_3)*	45	---
Phenols	0.001	---
Selenium (Se)	---	0.01
Silver (Ag)	---	0.05
Sulfate (SO_4)	250	---
Total Dissolved Solids (TDS)	500	---
Zinc (Zn)	5	---

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*In areas in which the nitrate content of water is known to be in excess of the listed concentration, the public should be warned of the potential dangers of using the water for infant feeding.

†Varies with average maximum air temperature.

BIOLOGICAL STANDARDS

Sample Examined	Limits
Standard 10-ml portions	Not more than 10 percent in one month shall show coliforms.†
Standard 100-ml portions	Not more than 60 percent in one month shall show coliforms.†

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†Subject to further specified restrictions.

RADIOACTIVITY STANDARDS

Source	Recommended Limits, Picocuries per Liter
Radium-226	3
Strontium-90	10
Gross Beta Activity	1,000

TABLE 14. GUIDE FOR EVALUATING THE QUALITY OF WATER USED FOR IRRIGATION (Todd, 1970)

[MPN is most probable number. Sodium adsorption ratio is defined by the formula $SAR = Na/\sqrt{(Ca + Mg)/2}$, where the concentrations are expressed in milliequivalents per liter. Residual sodium carbonate is the sum of the equivalents of normal carbonate and bicarbonate minus the sum of the equivalents of calcium and magnesium.]

Quality Factor	Threshold Concentrations[*]	Limiting Concentration[†]
Coliform Organisms, MPN per 100 ml	1000[‡]	[§]
Total Dissolved Solids (TDS), mg/l	500[‡]	1500[‡]
Electrical Conductivity, µmhos/cm	750[‡]	2250[‡]
Range of pH	7.0-8.5	6.0-9.0
Sodium Adsorption Ratio (SAR)	6.0[‡]	15
Residual Sodium Carbonate (RSC), meq	1.25[‡]	2.5
Arsenic, mg/l	1.0	5.0
Boron, mg/l	0.5[‡]	2.0
Chloride, mg/l	100[‡]	350
Sulfate, mg/l	200[‡]	1000
Copper, mg/l	0.1[‡]	1.0

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[*] Threshold values at which irrigator might become concerned about water quality and might consider using additional water for leaching. Below these values, water should be satisfactory for almost all crops and almost any arable soil.

[†] Limiting values at which the yield of high-value crops might be reduced drastically, or at which an irrigator might be forced to less valuable crops.

[‡] Values not to be exceeded more than 20 percent of any 20 consecutive samples, nor in any three consecutive samples. The frequency of sampling should be specified.

[§] Aside from fruits and vegetables which are likely to be eaten raw, no limits can be specified. For such crops, the threshold concentration would be limiting.

Quality classifications of water for irrigation usually stress certain ranges for sodium, total dissolved solids, and boron. A general guide for evaluating the quality of water used for irrigation is shown in Table 14.

Livestock Water

Poultry and farm animals can live on water of considerably lower quality than human beings. Quality criteria depend on factors such as the type of animal and its age, climate, and feeding regimen. A general guide for evaluating the quality of water used by livestock is shown in Table 15.

TABLE 15. GUIDE FOR EVALUATING THE QUALITY OF WATER USED BY LIVESTOCK (Todd, 1970)

Quality Factor	Threshold Concentration*	Limiting Concentration†
Total Dissolved Solids (TDS), mg/liter	2500	5000
Cadmium, mg/l	5	
Calcium, mg/l	500	1000
Magnesium, mg/l	250	500‡
Sodium, mg/l	1000	2000‡
Arsenic, mg/l	1	
Bicarbonate, mg/l	500	500
Chloride, mg/l	1500	3000
Fluoride, mg/l	1	6
Nitrate, mg/l	200	400
Nitrite, mg/l	None	None
Sulfate, mg/l	500	1000‡
Range of pH	6.0-8.5	5.6-9.0

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*Threshold values represent concentrations at which poultry or sensitive animals might show slight effects from prolonged use of such water. Lower concentrations are of little or no concern.

†Limiting concentrations based on interim criteria, South Africa. Animals in lactation or production might show definite adverse reactions.

‡Total magnesium compounds plus sodium sulfate should not exceed 50 percent of the total dissolved solids.

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APPENDIX

METRIC CONVERSION TABLE*

Non-Metric Unit	Multiply by	Metric Unit
inch (in)	25.4	millimeters (mm)
feet (ft)	0.3048	meters (m)
miles	1.60934	kilometers (km)
acres	0.404686	hectares (ha)
grains	64.79891	milligrams (mg)
gallons (gal)	3.7854	liters (l)
pounds per square inch (psi)	0.0680460	atmospheres (atm)
parts per million (ppm)	1	milligrams per liter (mg/l)
gallons per minute (gpm)	3.7854	liters (l) per minute
gallons per hour (gph)	3.7854	liters (l) per hour

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*English units were used in this report because the data obtained were not available in metric units.